INDUSTRIAL MICROSCOPY

Industrial Microscopy

By

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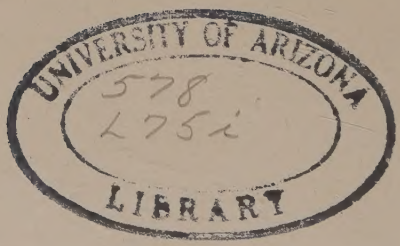

TO MY WIFE
WHOSE COURAGE, LOYALTY AND
SPIRIT OF SELF SACRIFICE
HAS MADE IT POSSIBLE
THIS VOLUME
IS AFFECTIONATELY
INSCRIBED

119447

PREFACE

SINCE the early eighties when the work of H. Behrens at the Polytechnic School in Delft, Holland, received world-wide recognition, CHEMICAL MICROSCOPY has had a slow but steady growth in European and American universities. In 1926 at least seven American institutions of higher learning had departments of chemical microscopy definitely established. The classes were small but enthusiastic. At that time these laboratories represented an investment of at least sixty thousand dollars. The most important of these was at Cornell University under the able direction of Dr. E. Chamot, who more than any one else has been responsible for the development of this particular field in America.

At Columbia University where the author introduced the work in the summer of 1925 at the request of Prof. D. D. Jackson, Head of the Department of Chemical Engineering, the classes consisted very largely of college professors who desired intensive instruction in order that during the summer months they might secure sufficient technique to carry on the work after returning to their respective institutions. At their request I have published this combination of text and laboratory outline, illustrated with photomicrographs of crystalline precipitates used for the detection of most of the elements, and also many raw materials entering industry.

There was a need for such a book. The English translation of Behrens' early work had been out of print for many years. His later books written with Kley as co-author were illustrated with drawings but were in German. The two editions of Chamot's *Elementary Microscopy* carried many illustrations of apparatus but none of the crystalline precipitates. For this reason the author has only a few illustrations of equipment, but many of the crystals as they actually appear when the tests are made.

Since the demand for such a book is necessarily limited some consideration had to be given to the size, selection and the arrangement of illustrations in order to reduce the cost. For this reason some of the plates do not come immediately with the subject matter they illustrate. This is unfortunate, but the high cost of separate engravings made such prohibitive. No attempt has been made to compete with special texts on textiles, alkaloids or alloys.

Merely the fundamentals of procedure in the control of some of the more important industries are given with the belief that when the student has become proficient in these he can strike out for himself and apply them to problems as they come up. In collecting material the author has taken the viewpoint that he is the "heir of all the ages" and has tried to place in one volume the best work that has been done during the last fifty years both here and abroad.

The test limits given are those announced by Behrens. They were checked in several instances and found to vary somewhat with the individual worker. Since chemical microscopy is an art as well as a science, too much dependence must not be placed upon the values given.

The *chemist* and *engineer* should become more familiar with the use of the microscope, which enables one to see if necessary more than a thousand times as well as his comrade who scorns its use. The writer has visited the laboratories of many of the greatest American universities and found the departments of qualitative analysis struggling along with equipment and methods used a hundred years ago, consuming hours and dollars in analysis when only minutes and cents were necessary.

These men, because in industry modern analytical microscopic methods are replacing many old familiar analytical methods, will probably be harsh critics. To the students who have to withstand the drudgery of qualitative analysis the newer methods will be welcomed. It is for these that the book is primarily written, for it is they who will be the professors of tomorrow.

In the actual labor of preparation much valuable assist-

ance has been given. The author wishes to give thanks to all of his former students who gave a helping hand, and especially to Dr. Warren of William and Mary, Professor Jones of Auburn, and Professors Albers and Herndon of Eastern Kentucky State. The personal interest shown by Bush-Krebs Company of Louisville, which made the engravings, and The William Byrd Press of Richmond has been an inspiration.

The author realizes that in writing this volume he is placing himself at the mercy of experts in many fields. However, if this volume should make the chemist appreciate a little more the work of the biologist and mineralogist the author will feel that his labors have not been in vain. Each with his microscope can meet on a common ground, can talk the same language and can view the wonders of creation among the rocks as well as among the flowers.

L. C. L.

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INDUSTRIAL MICROSCOPY

CHAPTER I

The Microscope

Early Lenses.—The microscope derives its name from the two Greek words, "mikros," meaning small, and "skopeo," to see. There is considerable evidence, however, to indicate that magnifying lenses were in use centuries before the period of classical Greece. Rock crystal,* found among the ruins of Nineveh, was exhibited by Sir David Brewster in 1852 at the British Association held at Belfast. Dutens is said to have possessed a lens found among the ruins of Herculaneum. At Athens, according to Aristophanes, globules of glass were sold by the grocerymen and called "burning spheres."

Ptolemy published in his "Optics" a table of the refractions which light makes at different angles of incidence when passing from air into glass. These values indicate that the glass of the ancients was not entirely unlike our own.

Pliny wrote that Myrmecides executed in ivory a square figure which a fly covered with its wings. A magnifying glass must have been used in this work as well as in the preparation of that Iliad of Homer written on parchment and comprised in a nutshell so ably described by Cicero. In "Natural Questions," Seneca wrote as follows:

"However small and obscure the writing may be, it appears larger and clearer when viewed through a globule of glass filled with water."

Simple Microscopes.—It was Zacharias Jansens who introduced the microscope to the public about the year 1590. Cornelius Drebell brought one of them to England. It was a copper tube six feet long and one inch in diameter, sup-

*Jabez Hogg, The Microscope, 1858.

ported by three brass pillars in the shape of dolphins. These were fixed to a base of ebony upon which the object was placed and corresponded to the stage of the microscope. The use of the instrument spread rapidly. Stelluti published a description of the parts of a bee, which he had examined under the microscope. Leeuwenhoek, Lyonet and Ellis studied many objects invisible to the eye by using lenses ground very convex. Their enthusiasm inspired many others to undertake and advance the work.

In 1656 Dr. Hooke published his "Micrographia Illustrata." He described how small glass globules could be

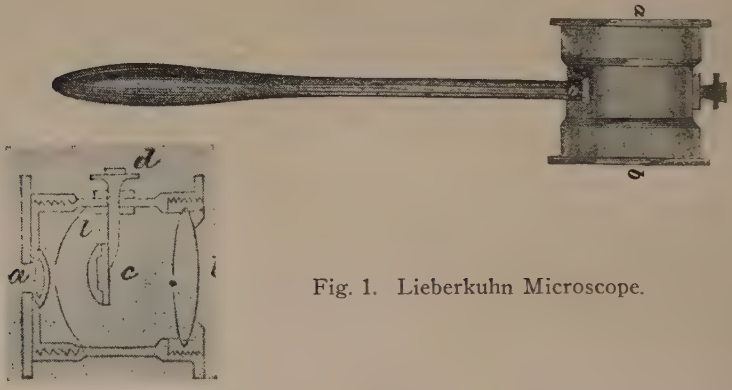

Fig. 1. Lieberkuhn Microscope.

made for purposes of magnification. Convex lenses had been used exclusively until then. He also suggested the use of immersion lenses. He had read Stephen Gray's description[1] of having built up a large drop of water containing animalcules which appeared greatly magnified when held close to the eye. Hooke, by dipping the glass globule in the water drop containing the animalcules, secured a "perfect view."

Dr. Nathaniel Lieberkuhn, of Berlin, made a very important improvement on the simple microscope in 1740.[2] He placed the lens in the center of a concave speculum of silver. When the silver was kept highly polished a bright

[1]Stephen Gray, Philosophical Transactions, 1696.
[2]Quekett's Practical Treatise on the Microscope.

light would be reflected upon the upper surface of the object. This made possible the more complete examination of opaque objects and was one of the earliest vertical illuminators. The apparatus was made from a brass tube about an inch long with a diameter of approximately an inch. At each end was a cap. (Fig. 1.) The cap at *"a"* carried a double convex lens of ½ inch focal length. The cap at *"b"* carried a condensing lens ¾ inch in diameter. At *"c,"* Fig. 1, the cross section shows a disk ⅜ inch in diameter. This is connected by a wire with the small knob at *"d."* At *"l"* is the silver speculum. By turning the knob at *"d"* the object mounted at *"c"* can be moved to or from the lens at *"a,"* and can be brought to a focus. The condensing lens at *"b"* concentrates the light on the silver speculum which in turn concentrates it on the object to be examined.

Leeuwenhoek made a large number of microscopes for various purposes. They were all simple and were made especially for the object to be studied. They were left as a gift to the Royal Society at his death. In a letter to the Society he said, "From my forty years experience, I have found that the most considerable discoveries were to be made with glasses of moderate magnifying power, which exhibited the object with the most perfect brightness and distinctness." In chemical *microscopy* we find the same to be true.

Early Compound Microscopes.—Dr. Hooke* described his compound microscope used in 1667. It was seven inches long and three inches in diameter. It had a deep eyepiece, a middle lens and an objective. Four draw-out tubes furnished additional magnification if desired. When a large area was to be studied he used all of the three lenses. If detail was sought, he removed the middle lens, for he found that the object was brightest when there were fewest refractions.

Our present method for the determination of the mag-

*Hooke, Micrographia, 1667.

nifying power of the microscope was described by Dr. Hooke. On the stage of his instrument he placed a scale accurately divided into minute divisions. On this he focussed carefully. When one division on the scale extended as far as thirty divisions on a similar rule, similarly divided, and examined with the naked eye, he knew that the magnification was thirty times.

Eustachio Divini's microscope was described at a meeting of the Royal Society in 1668. The tube was about 8 inches in diameter. The eyepieces were plano convex lenses and were so placed that they touched at the center of their convex surfaces. They were about four inches in diameter. It was equipped with a middle lens and an objective. Variations in magnification were obtained by using one or more of the four draw tubes which telescoped. When no draw tubes were used the instrument stood about 16 inches tall, and magnified forty-one times. For the second length the magnification was 90, for the third length 111, and for the fourth length 143 diameters.

Philip Bonnani published a description of a horizontal microscope in 1698. It was mounted in a cylindrical tube. Behind the stage was an illuminating device, consisting of a small tube with a convex lens at each end. A lamp placed beyond this furnished the light which was condensed on the object. This was one of the first substage condensers. The instrument was equipped with an objective, a middle lens, and an eyepiece.

In 1672 Sir Isaac Newton described to the Royal Society a microscope based on reflection. A concave spherical speculum of metal gave a reflected image, and an eyepiece furnished the magnification.

The pocket microscope had its beginning in 1742 and was the invention of Mr. Henry Baker, F. R. S.*

By the middle of the eighteenth century the microscope had been developed to such an extent that scientists were using it for many technical purposes. At this time Dr. Hill was employing it to study the growth of various types of

*Jabez Hogg, The Microscope, 1858.

trees. He endeavored to show how the construction of the cells and their arrangement might indicate uses for various woods. By physicians it was widely used.

Achromatic Lenses.—In "Microscopical Essays" for the year 1787, there is a description of a microscope invented by a Mr. Adams, and greatly improved upon by his son, George. It was constructed so that both opaque and transparent objects could be examined. This instrument was in general use until 1815, when Amici invented the achromatic improvement. Achromatic compound lenses received the attention also of Frauenhofer in Munich, Chevalier in Paris, and Tully in England. It was M. Selligues who first devised the objective composed of four achromatic compound lenses of two glasses each. On April 5, 1824, Mr. Tully constructed the first objective for a compound microscope ever made in England. It had a focal length of 9/10 inches, had three lenses and transmitted a pencil of light 18°.

In 1829 another great stride forward was made. Mr. Jackson Lister used Canada balsam to join together the plano concave lens to the convex. This prevented the loss of great quantities of light and thus increased the brightness of the field. They were made for uncovered objects, however, and the placing of a cover glass over the object caused them to be unsatisfactory. This difficulty was overcome by Ross who separated the anterior lens in the combination from the other two.

By the middle of the nineteenth century the London makers of microscopes had become unequalled. At that time the principal makers of the best instruments were Ross; Powell & Leland; and Smith & Beck. Since then the demand has very largely been supplied by the German and American made instruments, which have become more or less standardized.

The Analytical Microscope.—The modern industrial microscope must be more than a mere magnifier. A study of the catalogues of different optical companies will enable

one to select the type especially adapted to the work at hand. If funds are available at least one petrographical microscope should be in every microchemical laboratory. This instrument is equipped with polarizer and a condensing lens arranged so that either plane or converging polarized light can be employed. The instrument has a graduated rotating stage, an analyzer that slips in and out of the tube and a slot for the insertion of the selenite plate, quartz wedge, mica plate, etc. Above the analyzer is a Bertrand lens which aids in determination of interference figures.

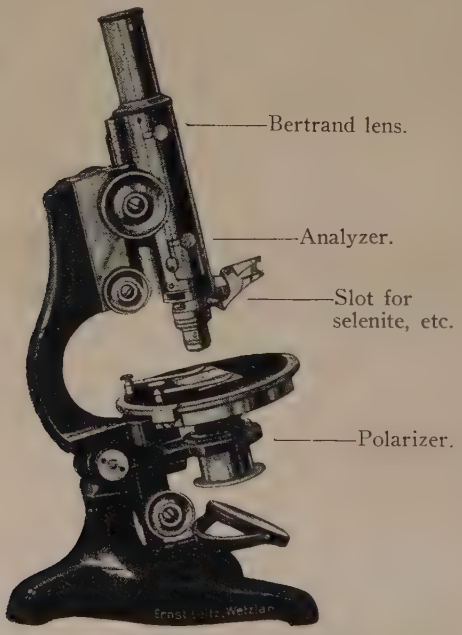

Fig. 2. Leitz Petrographical Microscope (Student Model).

When funds are limited and a cheaper type must be obtained a polarizing microscope, such as model "M" designed by Dr. E. M. Chamot of Cornell University is recommended.* The analyzer fits over the eyepiece and is graduated.

*Manufactured by Bausch & Lomb Opt. Co., Rochester, N. Y. E. Leitz also manufactures a chemical microscope.

A thorough knowledge of the use and care of the essential parts of the microscope is important. For this reason a brief discussion is given here.

Objectives.—The objective furnishes a magnified image of the object under examination. The objective, then, must be well constructed. Any fault that it has will be greatly magnified when this image in turn is magnified by the eyepiece. Its ability to furnish a well defined image is influenced by its magnifying power, resolving power, penetrating power, illuminating power, and its ability to give flat fields devoid of color fringes.

Magnifying Power.—This is dependent on the construction and arrangement of the lenses, and is marked on the objective. Marks in millimeters or inches indicate that the objective will give a real image, equal in size to that produced by a simple convex lens whose focal length is the distance marked. The shorter this distance the greater will be the magnification. If a lettering system is employed A would signify a lower magnification than B.

Illuminating Power.—The illuminating power of an objective is its ability to grasp light. It is obvious that a front lens of large diameter will admit more light than one whose diameter is small. Light may be considered as entering the objective in the form of a cone, the diameter of whose base is equal to that of the front lens, and whose apex is a point in the object lying in the optic axis of the microscope. The angle between the edges of this cone is called the *angular aperture.*

Experience has shown, however, that this is not a true measure for the light grasping power of objectives. A more exact measure would be the sine of ½ the angle of aperture multiplied by the refractive index of the medium into which the front lens of the objective dips. This value is known as the numerical aperture.

$$\text{N. A.} = \text{n. sin } \tfrac{1}{2} \text{ angle of aperture.}$$

Nelson* has shown that when the illuminating power is calculated from the equation, Ill. Power $= \left(\frac{\text{N. A.}}{\lambda}\right)^2$ a correction should be made. The constant 1.3 was found to be the relationship between the theoretical and the actual available illuminating power. When the wave length of the light used is also considered, the equation then becomes:

$$\text{Av. Ill. Power} = \left(\frac{\text{N. A.}}{1.3\,\lambda}\right)^2$$

Resolving Power.—The resolving† power of an objective is its ability to distinguish clearly the minute details of an object. In terms of wave length and numerical aperture it may be calculated from the following equation:

$$\text{Res. Power} = \frac{2\ \text{N. A.}}{1.3\,\lambda}$$

Penetrating Power.—This is the ability of an objective to give clear and distinct images of objects appearing at the same time in different focal planes. It may be expressed as follows:

$$\text{P. Power}\ \frac{1.3\,\lambda}{\text{N. A.}}$$

Selecting Objectives.—It is obvious from the above equations that the illuminating power can be made greater by increasing the numerical aperture and using light of short wave length. The resolving power can be increased in the same manner. The penetrating power, however, must be increased by using a small numerical aperture and light of long wave length.

For very high magnifications oil immersion objectives must be selected. These objectives have a front lens of small diameter and therefore have no great light grasping power. This ability is increased by introducing between the lens and the cover-glass a liquid of high refractive index, into which the lens dips. This liquid will bend many light

*Nelson, J. Roy, Micro. Soc. 1906, 521.

†A test plate made by J. D. Möeller's Institute für Mikroskopie, Wedel i. Holstein, Germany, measures resolving power. It has twenty diatoms whose striations vary from 3.7 to 95.2 in 1/1000 of an inch.

rays toward the optic axis of the microscope and increase the available light.

For chemical investigations it is very important to select objectives with long working distance. This lessens the danger of dipping the lens into chemicals that might corrode. The *working distance* of an objective is the distance from the front lens to the top of the cover-glass, when in focus.

A COMPARISON OF COMMON APLANATIC OBJECTIVES (JOHANNSEN)

$\frac{\Delta}{F} = \frac{\text{[1]Optical tube length}}{\text{Focal length of objective}}$ 250 mm. $= \frac{\text{Distance of most distinct vision}}{\text{Focal length of objective}}$

No.	Manufacturer	Focus in mm.	N. A.	Free Working Distance mm.	Field of View mm.	Magnification $\frac{\Delta}{F}$	Magnification $\frac{250}{F}$
1 1/3″	Bausch & Lomb.	32	.10	38	4.8	4	8
1	Fuess	32	.10	31	4.5	.....	8
1	Reichert	30	.17	25	5	5	8
aa	Zeiss	26	.17	14	4.0	8	9.5
1	Seibert	25.4	.22	14	3.6	8.6	10
2	Leitz	24	.19	16	4	5.8	10.4
2	Fuess	22	.21	15	2.8	.....	11.3
2	Seibert	12.7	.26	4	2.2	14.2	20.0
AA	Zeiss	17	.30	7.5	2.5	.....	14.5
2/3″	Bausch & Lomb.	16	.25	7	1.85	1.6	15.6
802	Beck	16	.15	7.5	2.2	9	15.6
3	Leitz	16.2	.30	5.5	2.1	10.3	15.4
4	Leitz	10	.47	2	1.1	18.2	25
3	Seibert	8.5	.35	2.5	1.5	21.4	30
4	Reichert	8	.50	2.0	1.45	20.0	31
1/3″	Bausch & Lomb.	8	.50	1.6	.9	20	31
C	Zeiss	7	.40	1.8	.9	31	36
6	Leitz	4	.82	.42	.48	48	62.5
1/6 L	Bausch & Lomb.	4	.65	.6	.4?	43	62.5
1/6 S	Bausch & Lomb.	4	.85	.3	.4?	43	62.5
804	Beck	4	.71	.64	.50	44	62.5
6	Natchet	3.5	.90	.60	.....	80	71.0

CARE OF LENSES.—Only the softest lens paper should be used in wiping objectives and oculars. Scratches are often

[1]The optical tube length is the distance between the posterior focal plane of the objective and anterior focal plane of the ocular. It is less than the mechanical tube length.

made by using coarse cloth. Xylol is used to remove immersion oil from objectives. Some solvents are injurious to the mountings of the lenses. When focussing the microscope first lower the objective until it almost touches the preparation, then look into the microscope and gradually raise the tube until it is in focus.

Function of Oculars.—The ocular magnifies the inverted image produced by the objective. The degree of magnification is usually designated by 5X, 10X, etc. If they should happen to be marked by their equivalent focal length the smaller number would indicate the greater magnification. Oculars also collect and concentrate the light rays, which cause the magnified image to appear brighter. There are two general types of oculars, the Huygenian (negative), and Ramsden (positive).

Huygenian Oculars.—The function of the field lens (lower lens) is to concentrate light rays. In so doing it reduces the size of the image formed by the objective. This reduced image, however, is magnified by the eye lens (upper) and can be observed best at the eye point, a short distance above the ocular. The area of the field obtained is greatly influenced by the diameter of the diaphragm.

Eye Point.—Adjust the mirror so that the field will be flooded with light and hold over the ocular a piece of ground glass. If the room is not too bright a circle of light will appear on the glass. The circle of light will vary in intensity if the glass is raised and lowered. Select the position of greatest intensity. This is the correct position for the eye when using the microscope. The light disk, known as the *Ramsden circle,* should be about one millimeter in diameter. Its size will vary with the numerical aperture and the magnification of the microscope.

Ramsden Oculars.—This type of ocular is used with micrometers. The lens system is such that the real image is formed outside of the ocular, the *entire system* acting as a magnifier of the real image.

Selecting Oculars.—When penetrating power is desired it is necessary to use lower power objectives. This has to be remedied by using higher eyepieces. When resolving power is desired the reverse is true. It should not be forgotten, however, that any defect in the objective is greatly magnified by the ocular. When oculars are so constructed that they aid apochromatic objectives in overcoming aberration they are called *compensating,* and when they can be interchanged on the microscope without having to readjust the focus, they are termed *par focal.*

Special oculars are made to be used for projection work and also for measuring angles. The latter are called goniometer oculars and have a circle graduated in degrees.

Illumination.—When objectives of low magnifying power are used the mirror of the microscope in many instances will furnish sufficient illumination. When high power objectives are used which have small numerical apertures more light is essential. This is furnished by an Abbe condenser.

The Abbe Condenser.—The lens system of this device is so constructed that parallel light from the plane mirror is concentrated by the two lenses into a small pencil of light, a large part of which can enter the front lens of the objective. By partly closing the diaphragm the oblique rays from the sides are removed and axial light is obtained. If axial light is not desired it can be removed by inserting a metal stop under the diaphragm, which will permit only those rays that are moving obliquely to enter the objective. Axial light may also be removed by placing the finger under the condenser. Oblique illumination thus obtained is useful where a view of one side of an object is desired. It is helpful in determining refractive index.

When using the Abbe condenser in photomicrography it is often necessary to lower the condenser to prevent "blurring" of the image.

Aberration.—Aberration may be either spherical or chromatic, and makes satisfactory work impossible.

Unfortunately the lenses refract light, the rays at either extremity of the double convex lens being more refracted than those passing through the center. The result then is not a perfect focus but a series of focal points in the vicinity of the principal focus. If the lens remains uncorrected it will be difficult to obtain a good focus on the entire field at the same time. Lenses corrected so that they will give *flat* fields are called *aplanatic* objectives.

By partly closing the diaphragm so that the central rays only are admitted spherical aberration can be remedied, but there is a corresponding loss in light.

Chromatic aberration is due to the fact that light of different wave-lengths travels through glass with different velocities. Since white light is made up of various wave lengths it follows that there will not be a perfect focus unless the lens is corrected. This has been remedied by placing a double convex lens of crown glass in combination with a double concave lens of flint. When the correction is such that *two* different wave-lengths are brought to a focus the lens is called *achromatic;* when three rays are brought to a focus the lens is known as *apochromatic.*

Dark Field Illumination.—When the structure of the substance being examined is very transparent quite often the Abbe condenser will so flood the field with light that the object does not furnish clear contrasting outlines. This can be remedied by lowering the condenser slightly. In extreme cases a contrasting field can be obtained by means of a dark field illumination.

For dark field illumination oblique light must be employed. A drop of water is placed on the top of the condenser lens and upon this the glass slide with the preparation is laid. The device is so constructed that the oblique light strikes the surface of the cover glass at an angle greater than the critical angle and is reflected back again into the condenser, or into space. The field will appear dark, but each particle that is under examination will appear bright. This type of illumination is very valuable for

investigating exceedingly small objects whose index of refraction is about the same as that of the immersion liquid.

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CHAPTER II

Crystals

Formation.—In the language of the Greek philosophers "crystallos" meant ice, and they thought that quartz was a variety of ice. The name, "crystal," is now applied to any regular polyhedral form which a compound assumes due to its controlling internal forces at work when the substance passes from a liquid or gaseous state to that of a solid. A brief discussion of crystals will be helpful to the chemist or engineer.

Most solids are crystalline and show constant properties in parallel directions because in such directions there is a like arrangement of particles. When a substance crystallizes under ideal conditions the particles come to rest in the position of most stable equilibrium. This is called the crystal "*habit*" of the compound. When the crystallization is hurried it assumes the shape it can take the quickest in order to be most stable; or that phase which requires the least energy and consequently does not take up that phase of most complete equilibrium. The plane surfaces found on crystals offer the most complete resistance to solution. These adjacent surfaces, called faces, make definite angles with each other which will be constant and can be measured with considerable accuracy on a goniometer. Many investigators make use of this property in the identification of compounds.

In making a study of crystals, their facial angles, birefringence and refractive indices should be measured. Their behavior with polarized light and special reagents should also be noted.

Symmetry.—The relations between bounding planes in a crystal may be discussed from a standpoint of symmetry. This arrangement of like directions is usually designated by the terms, plane, axis, and center of symmetry.

A solid has a plane of symmetry when for each face, edge

or solid angle, there is another edge, face or solid angle in like position to this plane. A crystal is symmetrical to a plane when the plane so divides it that either half is the mirrored image of the other.

It has an axis of symmetry when on being revolved about some line through the center each group of faces is repeated 2, 3, 4, or 6 times on a complete revolution.

Most crystals are symmetrical to a point at their center. This is called a center of symmetry.

Axial Ratio.—In systems other than the isometric one of the horizontal axes is taken as a unit to which the others are compared. This is called the axial ratio. For sulphur (orthorhombic)

a : b : c as .8131 : 1 : 1:9034

For rutile (tetragonal)

a : c as 1:.64415 or simply .64415

Crystal Form.—A set of like faces growing on a crystal is called a crystal form. The cube, dodecahedron and octahedron are typical. The form may have as many as forty-

a—Cube.
d—Dodecahedron.
p—Octahedron.

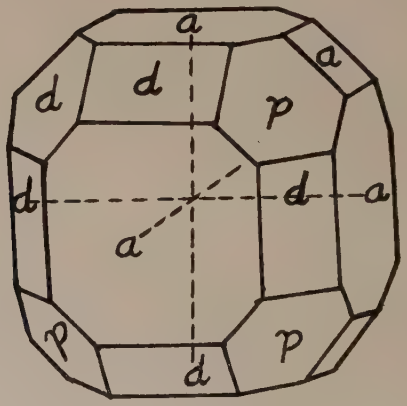


Fig. 4.

eight faces or as few as one, and several such forms may be present on a crystal at the same time. In Fig. 4 the cube, dodecahedron and octahedron are all present. Symbols are used to designate the location of these forms.

Symbols.—The most used symbols are the Weiss and Miller indices. These are based on the parameters of the plane surfaces and are the relative intercepts of the plane upon the crystallographic axes.

In the cube, Fig. 5, the three like crystallographic axes are designated for convenience by the letters a, a, and a. The face ABCD cuts one "a" axis at a unit distance. It is parallel to the other "a" axes and therefore cuts *them* at infinity. The Weiss indices for this face would therefore be

$$a : \infty a : \infty a$$

The Miller indices are the *inverted* coefficients of the Weiss. They would be in this instance 100, the coefficient

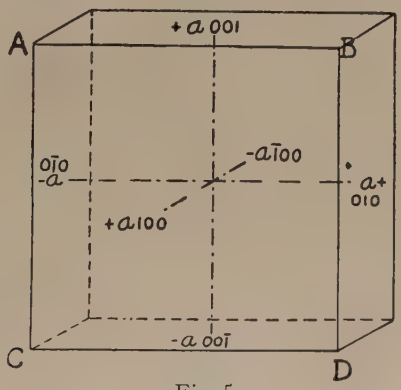


Fig. 5.

of "a" being $\frac{1}{1}$ and that of ∞ a being $\frac{1}{0}$.

In designating the faces by these indices the left, rear and bottom directions are considered negative.

Crystal Systems.—There are six crystal systems into which all crystalline compounds are grouped. On a basis of symmetry and their behavior with polarized light they may be described as follows:

Isometric

1. This system has three like diameters at right angles. Crushed fragments remain unchanged when observed with polarized light. No interference figures are ob-

tained, and only *one* refractive index. There are five classes.

1. *Normal Class*—

	Faces
Cube	6
Octahedron	8
Dodecahedron	12
Tetrahexahedron	24
Trisoctahedron	24
Trapezohedron	24
Hexoctahedron	48

2. *The Pyritohedral Class.*—There are two typical forms found in this division, the pyritohedron and the diploid. The pyritohedron has twelve faces of five sides, one of which is longer than the other four. It has three axes of two-fold, four of three-fold, and three planes of symmetry. Pyrite is an example.

   The diploid has twenty-four similar faces of four sides, each of unequal length. They are grouped in pairs, and on this account they are called diploids.

3. *Tetrahedral Group.*—Three axes of two-fold, four axes of three-fold, and six diagonal planes of symmetry.

   The simplest form in this class is the tetrahedron. Four equilateral triangles compose its faces. The crystallographic axes are found in a line joining the middle of the opposite edges. Tetrahedrons may be positive or negative.

   The other forms in this class are:

		FACES
Tristetrahedron	tetragonal	12
	trigonal	12
Hexatetrahedron		24

4. *The Tetartohedral Class.*—Crystals of barium nitrate and sodium chlorate may crystallize in this form. There are three axes of two-fold symmetry and four of three-fold symmetry. This group has neither a plane nor center of symmetry. The twelve-faced solid,

tetrahedral-pentagonal dodecahedron is representative of this group. It may be either right or left handed.

5. *The Plagiohedral Group.*—This is named from the spiral order of its faces. The forms found are the right and left pentagonal icositetrahedron. There are three axes of four-fold symmetry, four of three-fold symmery and six axes of two-fold symmetry. It has neither plane nor center of symmetry. Cuprite, halite, and sylvite are examples of this type of crystallization which is very unusual.

Uniaxial Crystals

(*Tetragonal and Hexagonal*)

2. Tetragonal.—This has one unique diameter which is the vertical "c" axis. Perpendicular to this are two other diameters which are like in length and in the arrangement of particles. These diameters may be taken perpendicular to the faces or perpendicular to the edges as the case may be. If the faces are referred to the two equal axes at right angles to the edges the prism is considered a *first order prism.* The prisms of the first order are parallel to the "c" axis, and cut both of the other two. If the two equal axes are selected that are normal to the faces, the prism is of the *second order.* The face of a second order prism is parallel to the vertical and also to the other horizontal axis.

Crushed fragments give parallel extinction with polarized light except when viewed in the direction of the "c" axis. In this direction they are isotropic. When grown from solution they appear as squares or rectangles, which may or may not have pointed ends. They give uniaxial interference figures. There are 7 classes.

1. *Ditetragonal Bipyramidal.*—This consists of a double, eight-sided pyramid whose faces cut the *c* axis and one *a* axis, but will meet the third axis only if extended.
2. *Ditetragonal Pyramidal.*—(Double eight-sided pyramid.)

3. *Tetragonal Bipyramidal.*—This has eight faces. Each of the four upper faces has a similar face below it in the same vertical plane.
4. *Tetragonal Pyramidal.*—This may be considered one of the halves of the tetragonal bipyramidal if it were cut in the horizontal plane where the two pyramids meet.
5. *Tetragonal Sphenoidal.*—(Faces present in alternate octants only.)
6. *Tetragonal Trapezoidal.*—This consists of a double pyramid composed of eight similar faces, each a trapezoid. The four lower faces, however, do not lie in the same vertical plane as the upper.
7. *Tetragonal Bisphenoidal.*—This has neither plane or center of symmetry. The vertical axis is one of two-fold symmetry. The two upper faces are not in the same vertical plane as the lower. (Rare.)

3. The Hexagonal System.—The hexagonal system is divided for convenience into two main divisions, the hexagonal and the rhombohedral. The crystals of the hexagonal division occur usually in the form of hexagonal prisms or double pyramids. These may be of either the first or second order as in the tetragonal system. With polarized light crushed fragments behave like tetragonal crystals. When grown from drops of solution hexagonal crystals usually develop first on end and appear as hexagons. There are 5 classes to the Hexagonal Division.
   1. *Normal* Class. Beryl is typical of this type of crystallization. It has one axis of six-fold symmetry, and six axes of two-fold symmetry. There is one horizontal and six vertical planes of symmetry. The forms that may be found in this class are the prism, pyramids of the first and second order, basal pinacoid, dihexagonal prism and pyramid.
   2. *Dihexagonal Pyramidal.*—Zincite is an example of this class. It has no horizontal plane of symmetry, no center of symmetry and no horizontal axis of two-fold

symmetry. Such a crystal is called *hemimorphic,* meaning half.

3. *Hexagonal Bipyramidal.*—Apatite illustrates this class. The only plane of symmetry is the plane of the horizontal axes.

4. *Hexagonal Pyramidal.*—This class is shown in nephelite. It is hemimorphic (one-half) to the hexagonal bipyramidal. It has no horizontal plane of symmetry. The vertical axis is one of six-fold symmetry.

5. *Hexagonal Trapezohedral.*—This has six horizontal axes of two-fold symmetry but no plane of symmetry. It is composed of two pyramids of six faces each. Each face is a trapezoid. The upper and lower faces do not lie in the same vertical plane.

Rhombohedral Division.—This division is subdivided into five classes. It has a vertical axis of three-fold symmetry which is characteristic of the group. The most important class in this group is the rhombohedral of which calcite is an example. In addition to the five classes described there are two others, the trigonal bipyramidal, of which there are no crystal representatives; and also the trigonal pyramidal, which is hemimorphic, and which is represented by the crystals of sodium periodate.

1. *Trigonal Class.*—This has three horizontal axes of two-fold symmetry, one horizontal plane of symmetry and three vertical planes of symmetry. The class has one member, the rare mineral, benitoite.

2. *Rhombohedral Class.*—Calcite crystallizes in this class. It has many other representatives such as hematite, corundum, chabazite, etc.

3. *Rhombohedral (Hemimorphic) Class.*—This is represented by tourmaline. There is no horizontal axis of symmetry. The vertical axis is one of trigonal (three-fold) symmetry. It has six faces.

4. *Tri-rhombohedral Class.*—This has a vertical axis of three-fold symmetry, a center of symmetry but no

planes of symmetry. It has six faces. The upper and lower faces are not in the same vertical plane. There are a number of examples of this crystallization. It is found in willemite, dolomite and ilmenite.

5. *Trapezohedral Class.*—Quartz is the best example of the class. There are no planes of symmetry, and no center of symmetry. It has three horizontal axes of binary symmetry, and the vertical axis is one of trigonal symmetry. Cinnabar is another member of this class.

Biaxial Crystals

4. Orthorhombic. — The orthorhombic system has three diameters meeting at right angles, unlike in length and in arrangement of particles. Any one of these three diameters may be selected as the vertical "c" axis. The longer of the other two is called the macro axis and is designated by the letter "b." The shorter of the lateral axes is called the brachy axis and is designated by the letter "a." In writing the axial ratio, "b" is taken as the unit to which the others are referred. Crushed fragments give parallel extinction in three directions when viewed with polarized light. They also may give biaxial interference figures. Brachy and macrodomes may be present.[1]

1. *Normal Class.*—Barite furnishes an excellent example of this type. It is a double pyramid with four faces in the upper half and four in lower half and in the same vertical plane.

2. *The Hemimorphic Class.*—This has one axis of twofold symmetry and two unlike planes of symmetry. Calamine is an example of this type of crystallization.

3. *The Sphenoidal Class.*—This is best illustrated by means of a crystal of Epsomite. It has three axes of

[1]When two faces are parallel to the longer horizontal axis the form is called the *macrodome.* When parallel to the shorter axis it is called the *brachydome.*

two-fold symmetry but neither plane nor center of symmetry.

5. MONOCLINIC.—This system has three unique diameters. Two of these are at right angles to each other. The third diameter is oblique. The acute angle is designated by the Greek letter "β." When fragments of monoclinic crystals are examined with polarized light, they should be rolled gently under the cover glass so that their behavior can be noted in several positions. When they give parallel extinction, the section is parallel to the b crystal axis. The crystal will give parallel extinction in two directions and oblique in the third. There will be three refractive indices. Crushed fragments will give biaxial interference figures. There are three subdivisions of this system.
   1. *Normal Class.*—In this class can be found one plane of symmetry and one axis of two-fold symmetry. Crystals of this type of crystalliaztion are epidote and gypsum. The forms occurring in this class are:
      1. Orthopinacoid.
      2. Clinopinacoid.
      3. Prisms.
      4. Basal pinacoids.
      5. Orthodomes, faces parallel to the ortho axis b, and meeting the other two axes.
      6. Clinodomes, faces which are parallel to the clino axis "a."
      7. Pyramids.
   2. *Hemimorphic Class.*—Sugar crystals and tartaric acid are types, having a single axis of binary symmetry and no plane of symmetry.
   3. *Clinohedral Class.*—This has no axis of symmetry and only one plane. Clinohedrite ($H_2 Ca Zn Si O_5$) is the representative of this class among minerals.
6. TRICLINIC SYSTEM.—This system has three unique diameters which are not only different in length but also in the arrangement of particles. None of these make angles of ninety degrees with each other.

One of these directions is selected as the vertical axis. The one sloping down to the observer is called the "a" axis and the other is called the "b" axis. Crushed fragments give three refractive indices, biaxial interference figures, and oblique extinction in all directions. There are two classes.

1. *Normal Class.*—It has only a center of symmetry. The possible forms that could occur are the following:
   1. Macropinacoid.
   2. Brachypinacoid.
   3. Base.
   4. Prism.
   5. Marcodomes.
   6. Brachydomes.
   7. Pyramids.

   This crystallization is the habit of albite.

2. *Asymmetric Class.*—This has no symmetry. Its form has one face only. Calcium thiosulphate ($CaS_2O_3 . 6H_2O$) is an example of this. There are no mineral examples known.

Optic Axes.—Uniaxial crystals appear isotropic with polarized light if they happen to be lying in such a way that light is entering in the direction of the vertical "C" axis. This direction in which there is no double refraction is called the *optic axis*. Biaxial crystals have two such directions. They lie in the planes of minimum index of refraction α and maximum γ. The intermediate index of refraction β lies in a plane perpendicular to that in which the two optic axes lie and is known as the optic normal. The angle formed by the optic axes is known as 2V. The actual measurements are greater when observed with the microscope and are called 2E. The true angle is calculated from the observed angle by the formula:

$$\text{Sin V} = \frac{\text{Sin E}}{\beta}$$

The observed value for 2E will change with the tempera-

ture and the wave length of light used. If the fragment under observation is immersed in a liquid another factor is introduced depending upon the index of refraction of the liquid used. When such is the case the symbol 2H is used instead of 2E and the wave length of light employed is recorded.

The relation between the three refractive indices[1] and the interior optic angle 2V can be calculated from the following equations:

$$\text{Cos}^2 V = \frac{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}{\frac{1}{\alpha^2} - \frac{1}{\gamma^2}} \quad \text{or} \quad \text{Tan}^2 V = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}$$

Colloidal Growths.—When crystallization is taking place in the presence of some substance like gum arabic, gelatin or other colloidal preparation, very interesting developments occur. Instead of crystallizing out in their usual habit, the crystals form many curved and twisted groups of branches growing out in all directions.

In the presence of such substances characteristic crystal growth can seldom be attained.

Pleochroism.—Some crystals have the power to absorb light of certain wave length. The color of crystals is the complement of that color which has been absorbed. This power of a crystal may sometimes vary with the crystallographic direction through which light happens to be vibrating through the crystal. This causes the change in color as the crystal is rotated on the stage of the microscope when the analyzer is removed. When a fragment shows a two-color change it is called *dichroic,* when it has a three or more color change it is called pleochroic.

Extinction Angles.—The angle which some crystallographic direction makes with one of the vibration directions in the crystal is called the extinction angle. The one

[1]Dana's Textbook of Mineralogy, 1921.

taken is usually the *smallest* angle that can be found. To determine the value of an extinction angle bring some crystallographic direction parallel to one of the cross hairs of the microscope and read the stage. Then rotate the crystal until the position of maximum darkness is reached. (The selenite plate will aid in determining when this point is obtained.) Then read the stage again. The difference will be the extinction angle. The average of a number of readings should be taken. Some authorities use the largest average angle instead of the smallest.

Crystals With Polarized Light

Double Refraction.—This can be clearly demonstrated by means of a clear crystal of calcite. If this is placed over a black mark on a piece of paper *two* marks will appear instead of one. The light rays entering the crystal are broken up into two rays, travelling with different velocities. This property is common to anisotropic crystals. The amount of separation of the two refracted rays indicates the strength of the double refraction. This is called *birefringence.*

In some crystals, however, only one of these rays may emerge. This is well illustrated with a crystal of tourmaline. When light enters a thin section of this mineral, which is cut parallel with the c axis the light is broken up

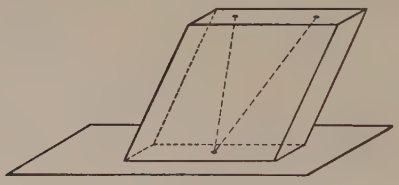


Fig. 6.

into two rays. One of these will be vibrating parallel to the c axis and will emerge. The other will lie in the plane of horiozntal axes and be absorbed. The light that emerges will be vibrating in one plane only, and is called *polarized light.*

Polarized Light.— In 1828 William Nicol invented what is now called the nicol prism for securing polarized light by double refraction. He used a cleavage of calcite (Iceland spar) with a length about three times its width. The faces that made angles of 70° 52′ and 109° 8′ to the side QN were ground down until the angles were 68° and 112° respectively. The prism was then cut through by a plane PN at *right angles* to these ground faces. After careful polishing the parts were cemented together with Canada balsam which has a refractive index of 1.54. This is less than one of the refractive indices (1.658) of calcite, and lies near 1.516, the other refractive index. When a ray of light enters the prism at R it is immediately broken up into two rays on account of the doubly refracting nature of calcite. One ray OR which we call the ordinary ray, whose index of refraction is 1.658, strikes the surface PN at an angle *greater* than the critical angle and is therefore reflected back into the crystal. It finally emerges and is absorbed into the black walls of the microscope.

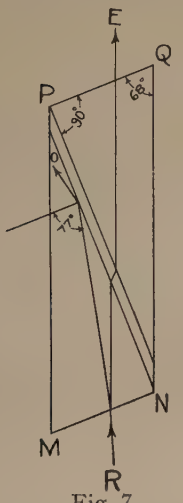


Fig. 7.

The ray RE, which is called the extraordinary ray and whose refractive index, 1.516, lies very close to 1.54 of Canada balsam, is simply diverted a little and emerges vibrating in one plane. A combination of two such nicols, between which transparent crystals can be examined, is called a conoscope or polariscope. When the two prisms have been so rotated that their planes of vibration are at *right angles* they are said to be *crossed.* The light that emerges from the lower nicol, the polarizer, will be completely extinguished by the upper nicol which is called the analyzer.

Anisotropic Crystals with Polarized Light.—Doubly refracting crystals not only refract light but may also polarize the two rays in planes that are at right angles to each

other. When such crystals are rotated between crossed nicols they will appear alternately light and dark. In Fig. 8, BC and DE are the two directions of vibration in the crystal. The lines PL and AN are the directions of vibration for the polarizer and analyzer. The light, plane polarized, emerges from the polarizer vibrating in the direction

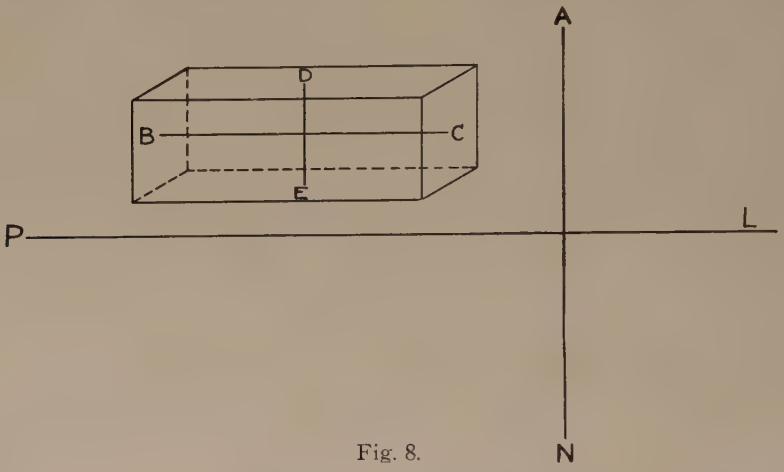


Fig. 8.

PL. On striking the crystal it will vibrate in the direction BC. In this position the crystal's vibration directions are parallel to those of the analyzer and polarizer. A ray vibrating parallel to BC *cannot be resolved into another at right angles.* Since there are no vibrations parallel to DE the crystal will appear dark, the rays vibrating parallel to BC being diverted by the analyzer. If the crystal is rotated the darkness will appear every 90°. When the crystal becomes dark it is said to be extinguished.

If the stage is turned only 45° the fragment will appear brightest, and will grow dimmer as the angle approaches the 90° limit.

In Fig. 9, MN and PL are the vibration directions of the analyzer and polarizer. Light, plane polarized by the polarizer and vibrating parallel to the plane PL enters the crystal and is immediately resolved into *two* rays, AB and

CD, which coincide with the vibration directions of the crystal. These two rays travel on and meet the analyzer where they must vibrate parallel to MN and PL. The analyzer resolves AB into two such rays, AE and BE, vibrating parallel to PL and MN respectively. The ray CD is likewise resolved into CF and FD. The rays, AE and

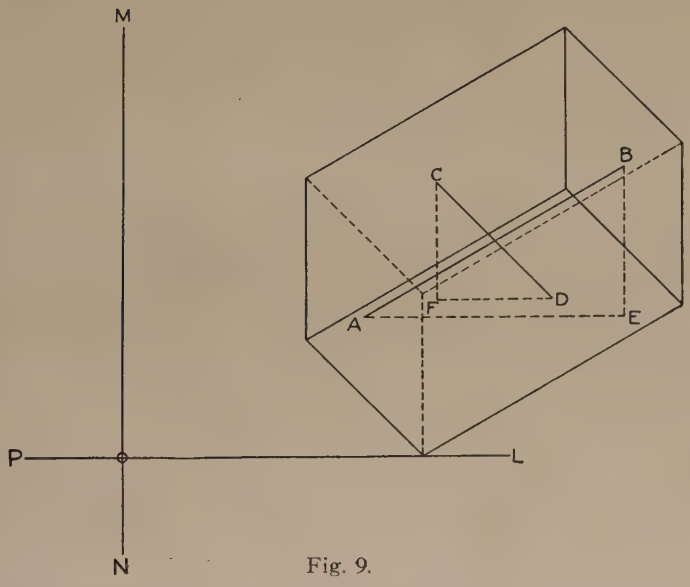


Fig. 9.

FD, vibrating in the direction PL, are diverted by the analyzer but CF and BE can emerge and in this oblique position the crystal will appear bright. If the crystal is thin it will be colored. These are called interference colors.

Interference Colors.—When thin fragments of a doubly refracting crystal are examined under the microscope with polarized light bright colors may be observed. These are known as interference colors, and are caused by the removal of some particular color from white light, on account of interference. Since the crystal is doubly refractive, the two rays will travel with different velocities, and will emerge in different phases. Waves having different phases will cause interference, which may result in the ex-

tinction of light of some particular wave length. The color complementary to this results.

If the fragment has a tapering edge a series of different colored bands may be observed on the sloping side. These will generally appear in the order of violet, blue, green, yellow, orange, red. If the sloping edge is sufficiently long and thick these colors may be repeated several times. Each of these repetitions is called an *order*. The order can be determined by means of the quartz wedge, which is so cut that it behaves like a crystal fragment with a tapering edge.

The Quartz Wedge.—A crystal of quartz is cut in the shape of a long thin tapering wedge. If it has been cut with its long direction perpendicular to the c axis of the quartz, the direction of the faster ray is indicated by X. If the long direction is cut parallel to the c axis, the letter Z means that this is the direction of the slower ray.

In all petrographical microscopes there is a slit in the tube above the objective through which the wedge can be pushed at an angle of 45° to the planes of vibration of the nicols. As it is pushed gradually in the slit different shades of color will appear and repeat themselves several times, as the interference increases with the thickening of the crystal wedge.

The Order of a Color.—The crystal will be brightest when its planes of vibration are making an angle of 45° with those of the polarizer and analyzer. Turn the crystal to this position and then introduce the quartz wedge which will either decrease or increase the double refraction of the crystal. If the wedge increases the double refraction the original interference color of the crystal will rise, in its order, red will become blue, blue become green, etc. If the wedge decreases the double refraction the original red color will change to yellow, yellow to green, etc. In the first instance the wedge makes the crystal act as though it had been thickened, and in the second case, thinned. THE CRYSTAL MUST BE ARRANGED SO THAT WHEN THE WEDGE IS PUSHED IN THE INTERFERENCE COLOR WILL FALL IN ITS

ORDER. As the wedge is pushed gradually in the succession of colors that occur as the double refraction is decreased

1st Order.	2nd Order.	3rd Order.	4th Order.
Iron Gray.	Violet.	Blue.	Pale Red, Violet of 4th order.
Gray.	Blue.	Green.	
Pure White.	Blue-Green.	Pale Green.	
Faint Yellow.	Yellow-Green.	Pale Rose Red.	
Yellow.	Yellow.	Reddish Violet.	
Orange.	Orange.	Red of 3rd order.	
Red of 1st order.	Red of 2nd order.	Green.	
	Violet.		

is very marked. The point will finally be reached where gray of the first order appears. This is when the wedge is said to compensate the crystal. Whatever gain the faster ray had over the slower in the crystal has been eliminated by the wedge.[1] The *order* of the original color is determined by noting what succession of colors occur until gray of the first order is reached. Above is shown the colors as they appear in their several orders. The thickness of the wedge increases from .033 mm. at pure white to .228 for red of the fourth order.

THE SELENITE PLATE.—The selenite or the mica plate can be used to roughly determine the color order, and when the thickness of the crystal is known the approximate birefringence of the crystal can be estimated. In the following table[2] the word "Bright" means definite colors and "High" signifies faint tints grading into white.

	Birefringence
HIGH ORDER—Not much changed by mica plate either in the crossed or parallel position	> .06
BRIGHT B—The crystal gives bright colors in both positions when the gypsum plate is used. The mica plate gives distinctly different tints for the crossed and parallel positions	.024—.06

[1]See Johannsen, Manual of Petrographic Methods.
[2]Moses and Parsons, mineralogy, Crystallography and Blowpipe Analysis.

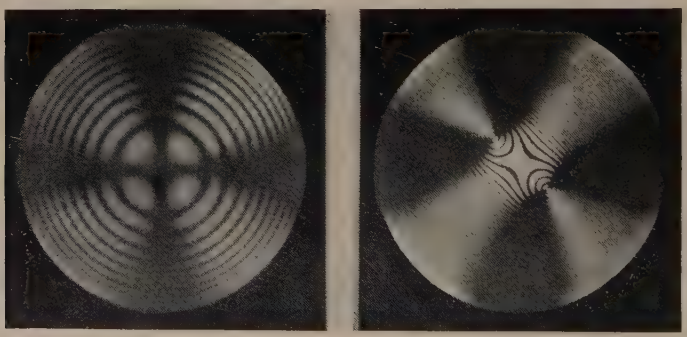
BRIGHT A—The crystal is made white, gray or black for both the parallel and crossed positions ..... .008—.024

GRAY OR WHITE—The crystal is made blue or purple by the gypsum plate for parallel position and yellow for crossed position. < .008

BLACK—The crystal remains unchanged by rotation between crossed nicols..... 0

The practical use to which the color order of crystals can be employed is illustrated in the detection of anhydrite in the presence of gypsum. Gypsum gives with the selenite plate a Gray or White color order and sometimes a Bright A. Anhydrite, on the other hand, gives Bright B colors. To detect anhydrite in the presence of gypsum by chemical means would be extremely difficult.

INTERFERENCE FIGURES.—In routine work with mineral sections interference figures are of real importance and when they can be obtained with crystal fragments may be the deciding factor in placing the crystal in the uniaxial or biaxial group.



Uniaxial Interference Figure. Biaxial Interference Figure.

Fig. 3.

UNIAXIAL FIGURES.—When basal sections of tetragonal or hexagonal (uniaxial) crystals are examined with a 4 m.m. objective and converging polarized light the Bertrand lens

being pushed in, a dark cross (isogyres) will be observed lying on colored rings. Each arm of the cross is narrow at the center and widens as the distance from the center is increased. If monochromatic light is used the colored rings will become dark, due to the retardation at those points of one or more wave-lengths. When white light is used the complementary color of the wave-length of light removed at that point appears. The number of rings will depend on the strength of the double refraction and the thickness of the section.

The dark cross is due to the removal of light in the directions parallel to the vibration directions of the crossed nicols, the greatest intensity of light being at an angle of 45°. Between parallel nicols the cross will become white and the greatest darkness at the position of 45°.

Biaxial Interference Figures.—These are obtained from orthorhombric, monoclinic and triclinic crystals, when sections are cut at right angles to the acute bisectrix.

Since the optic axis of a crystal is that direction where vibrations occur with equal ease there will be no interference color. Along this direction the crystal will appear dark, but in other directions there will be interference due to retardations of one or more wave-lengths.

These retardations result in the formation of a biaxial interference figure consisting of two dark spots (points of emergence of the 2 optic axes) surrounded by dark oval bands if monochromatic light is used, colored if white light is used.

In addition to these isochromatic curves, dark brushes (isogyres) will appear and on rotating the stage they will become two hyperbolas revolving in the opposite direction from the stage.

Unfortunately it is seldom that a crushed fragment is so lying that interference figures can be obtained by the chemist, and for this reason no large amount of space is given to the subject. If the student so desires, optical companies can furnish special equipment to enlarge the interference

figure so that small fragments of crystals can be successfully studied.

Laboratory Exercises

1. (a) Examine with converging polarized light a section of calcite[1] cut perpendicular to the optic axis. Use a 4 mm. objective and the Bertrand lens.

   (b) Note the smallness of the interference figure if the eyepiece is removed and the Bertrand lens not employed.

2. When a good interference figure is obtained with the Bertrand lens push a mica plate in the slot over the objective. If the two "dots" in the interference figure lie at right angles to the vibration direction of the mica the calcite is positive. If they lie in the same direction the section is negative.
3. Repeat 2, using the gypsum plate, and note the results.
4. Repeat 2, using the quartz wedge.
5. Perform the same experiments on a biaxial crystal cut perpendicular to the acute bisectrix.
6. Examine the interference figure of gypsum by white light, then use various color screens.[2]
7. Secure sections of any of the following and check their optical properties with quartz wedge,[3] mica and gypsum plates.

	Biaxial	
Titanite	Mono.	+
Staurolite	Orthorth.	+
Chrysolite	Orthor.	+
Muscovite	Mon.	—
Topaz	Orthorth.	—

[1] W. Harold Tomlinson, Swarthmore, Pa., can furnish mineral sections.
[2] Johannsen—Manual Petrographic Methods, page 445.
[3] If the quartz wedge has *slow* vibration direction perpendicular to the long edge and is pushed in from S.E. to N.W. with thin end foremost the colors will move toward center in S.W. and N.E. quadrants in positive crystals and in negative crystals toward N.W. and S.E. quadrants. If wedge is cut with slow ray parallel to the long direction the reverse is true.

Uniaxial

Chabazite	Hex.	—	(Interference figure is confused.)
Beryl	Hex.	—	
Quartz	Hex.	+	
Zircon	Tetrag.	+	

Positive and Negative Crystals.— The direction of vibration of X (the faster ray) and Z (the slower ray) bisects the angles between the optic axes. The one bisecting the acute axial angle is called the acute bisectrix and the one bisecting the obtuse angle is called the obtuse bisectrix. Since either X or Z may bisect the acute angle it follows that sometimes X is the acute bisectrix and sometimes Z. The crystal is considered *negative* when X is the acute bisectrix. When it is Z the crystal is optically *positive*. The selenite plate also greatly aids in deciding when a crystal is positive or negative. The selenite itself will give a red color of the first order. If the selenite is introduced in such a way that the direction of its faster ray (X) parallels the vibration of the slower ray in the mineral, there will be a decrease in the order of the interference color. Under such conditions in two quadrants the red will become yellow. The other two opposite quadrants will change to blue because in this direction the faster and slower rays of the mineral coincide, causing the interference color to rise in its order. If the direction X of the sensitive tint makes a cross with a line joining the two blue areas the crystal is considered to be positive, if not it is negative.

The Mica Plate.— The mica plate may also be used to determine whether the crystal is positive or negative. It is made from a thin sheet of mica of such thickness that the faster ray emerges ¼ wave-length ahead of the slower ray. The direction of the slower ray (Z direction) is indicated by an arrow. The mica is mounted between thin plates of glass in such a way that it will fit into the slot just above the objective. When it is in this position the Z direction

makes an angle of 45° with the vibration planes of the crossed nicols.

Before the positive or negative character of a crystal can be determined a good interference figure must be obtained. When a good interference figure is gotten the mica plate is inserted in the slot. Two black arcs will lie in the direction of the Z vibration of the mica and will appear to have been drawn in toward the center. The other two will lie at right angles to the Z direction of the mica and will appear to have been pushed out. If the crystal is positive two black spots will appear close in toward the center in each of these last two quadrants. A line joining these would make a + sign. Under these conditions the crystal is considered positive. If the more distant arcs and black spots should lie in the two quadrants which coincide with the Z direction of the mica a line joining these would not cross but coincide with the Z direction, making a *minus* sign.

Refractive Index

Refraction.—Light travels in different media with different velocities. This produces refraction. In Fig. 10 oblique light is travelling from air into a glass prism, an optically denser medium, in which the velocity of light is only three-fourths as great as it is in air. When RA reaches the plane surface at A, the ray R_1C has reached only the point B. By the time this has reached the plane at C, RA has penetrated the glass a distance Ay, equal to three-fourths BC; R′A′ has penetrated as far as y′; etc. The line CD would represent the new wave front of the light rays in the glass. In glass of definite composition the ratio of BC, the speed in air, to Ay, the speed in glass would be a constant. This is called "n" the index of refraction.

$$\frac{\text{V in air}}{\text{v in glass}} = \frac{\text{BC}}{\text{Ay}} = \text{K} = \text{“n”}.$$

The refractive index is usually expressed as the ratio between the sines of the angles of incidence and refraction.

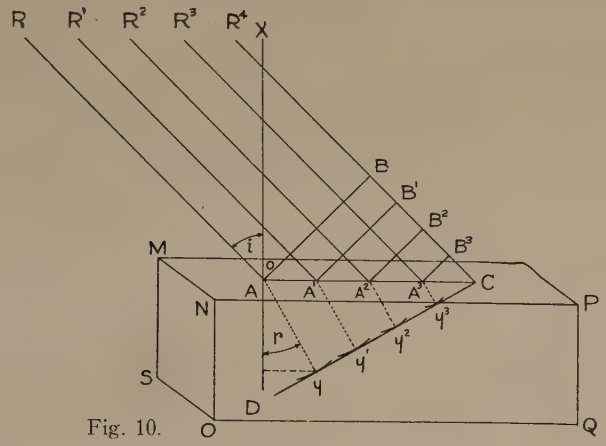


Fig. 10.

In Fig. 10, angle BAC is equal to RAX, the angle of incidence. Therefore $\frac{BC}{AC} = \text{Sin BAC} = \text{Sin i}$. Since angle ACy is equal to angle DAy, the angle of refraction, $\frac{Ay}{AC}$ (the Sin ACy) = Sin r.

$$\text{By Division } \frac{\frac{BC}{AC} = \frac{\text{Sin i}}{1}}{\frac{Ay}{AC} = \frac{\text{Sin r}}{1}} = \frac{BC}{Ay} = \frac{\text{Sin i}}{\text{Sin r}} = \text{“n”}$$

The refractive index of a pure substance is a constant. If this constant can be determined, it forms a valuable clue for the identification of many compounds.

Total Reflection.—If the incident ray coincides with the perpendicular RA in Fig. 11, no change of direction takes place. There is only a change of velocity as the ray goes from one medium to another. If an incident ray, such

as B′P should make an angle of 90° with RA, the equation for the refractive index would be

$$n = \frac{1}{\text{Sin } r} \qquad (\text{Sin } 90° = 1)$$

If the prism is made of crown glass of refractive index, 1.608 the value for r can be calculated from the equation

$$(1) \quad \text{Sin } r = \frac{1}{1.608}$$

For crown glass this angle of refraction is 38° 27′; for water it is 48° 31′; for the diamond it is 24° 25′. All substances that transmit light have a particular value for r

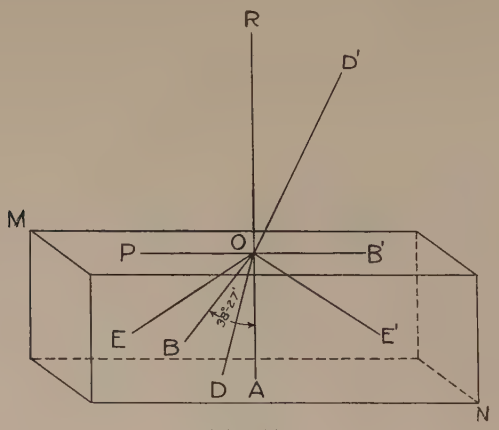


Fig. 11.

which will cause the light emerging from the crystal to make an angle of 90° with the normal RA. Angle AOB is 38° 27′, so the ray BO will emerge and pass along the direction OB′. The ray DO makes an angle *less* than 38° 27′, so it will emerge and vibrate in the direction OD′. The ray EO makes an angle with RA greater than 38° 27′ and *does not emerge at all.* On striking the surface at O it will be reflected back into the glass in the direction OE′ at the same angle at which it struck the surface. The angle at which this total reflection will take place is called the *critical angle.*

Gem stones are cut with flat top surfaces with inclined facets on the botttom. As light enters the stone from above it is reflected back from the sloping planes into the crystal, greatly increasing the brilliancy. The brilliancy of the stone also increases with the index of refraction.

Determination of Refractive Index.—Very complete lists of media[1] for refractive index determinations can be obtained from Johannsen, Manual of Petrographic Methods. Groth's tables carry a number of the refractive indices of crystals which can be used to determine the refractive index of liquids when an Abbe[2] refractometer is not available. Some of the more common are given below. It is more convenient to use crystals of the regular crystal system which have only one refractive index.

Refractive Index	Name
1.450	Potassium alum
1.490	Potassium chloride
1.544	Sodium chloride
1.571	Barium nitrate
1.640	Ammonium chloride
1.667	Potassium iodide
1.700	Ammonium iodide
1.755	Arsenic trioxide
1.95	Lead nitrate

The Immersion Method.—A few very small fragments of the crystal to be studied are placed on a glass slide, a drop of liquid of known refractive index is placed on the grains and the preparation covered by a thin cover glass. The condenser below the microscope should be lowered and the iris diaphragm closed so that only a bright pencil of light enters the objective. Focus carefully on a fragment and then raise the microscope tube. If the crystal is of lower refractive index than the liquid, a careful observer

[1]Wright's Series, Bulletin 158, Carnegie Institute.
[2]Chemische Krystallographie, Leipsic, 1906-10.

will notice that faint light bands in the crystal will move *outward* as the tube is raised. If the crystal is of higher refractive index the light in the crystal will move toward the center.

Oblique light[1] may also be employed in the immersion method. By placing the finger or a piece of cardboard between the mirror and the polarizer in such a way that one-half of the field is darkened oblique light can be obtained readily.

If the crystal under observation has a refractive index higher than the immersion liquid the light rays will be convergent on emerging from the crystal. One of these rays will miss the objective and the crystal will appear darkened on the *right*. If the crystal is of lower refractive index than the liquid the emerging rays will be divergent. The rays on the *left* will miss the objective causing a darkening of the crystal on that side. If both the crystal and liquid have the same refractive index the light will be on both sides of the fragment.

The behavior of air bubbles and fragments of lead nitrate in glycerine illustrates the phenomena very readily. Place a drop of glycerine on a glass slide, beat it up gently with the point of a glass rod until air bubbles appear. Then place in the drop a few small fragments of lead nitrate and cover the preparation with a thin cover glass. Focus first on the air bubble, using *axial light*. It will appear with a bright disk in the center. Now carefully raise the tube of the microscope with the fine adjustment. The light will move *outward* as the tube is raised, *inward* as the tube is lowered. Air has a lower refractive index than glycerine. Next focus on a fragment of lead nitrate, and observe the movement of the light as the tube is raised. In this case the light will move *inward*, and will move outward when the tube is lowered. The refractive index of lead nitrate is greater than that of glycerine.

Had the crystal of lead nitrate almost completely dis-

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[1]Wright, Oblique Illumination in Petrographic Microscopic Work; Am. J. Sci. (4) 35 (1913) 63.

appeared, then we would have considered that crystal and liquid had the same refractive index. In determination of index of refraction by the immersion method, we keep changing the liquid until this is the case. Liquids must be selected in which the solid being examined is not appreciably soluble.

Crystals of the regular crystal system (isotropic) have only one refractive index. Light travels in these crystals with the same velocity in all directions.

Crystals of the tetragonal and hexagonal systems have two indices of refraction. The arrangement of particles of matter in these systems is unlike in two directions. Light will travel with different velocities depending on which direction it happens to be moving. The higher refractive index is found in the direction of least velocity, and the lower refractive index in the direction of higher velocity. The difference between the lowest and highest refractive index of a crystal determines its *birefringence*. The Greek letter ω is used to designate the refractive index when light is moving *transverse* to the vertical axis, and ε is used when light is transmitted *parallel* to this direction. When ω is greater than ε the crystal is called *negative*. It is called *positive* when ω is less. The highest index for a negative mineral and lowest for uniaxial positive crystal is ω.

Orthorhombic, monoclinic and triclinic crystals present greater difficulties. These crystals possess three refractive indices. In addition to the maximum and minimum vibration there is an intermediate. The crystallographic axis of the orthorhombic crystals coincide with the directions of light vibration, but this is not true for the monoclinic and triclinic. The monoclinic has one crystallographic direction, the b axis, coincident with light vibration, and the triclinic has none. These directions of vibration are called, "*axes of elasticity*."[1] All three are at right angles to each other. Two are in the direction of maximum and minimum velocity. The third has the direction of the intermediate velocity and is perpendicular to the plane of the other two.

[1]Luquer, Minerals in Rock Sections. New York, 1898.

Refractive Index of Uniaxial Crystals.—After immersing the crystal to be examined in some medium of known refractive index, it is covered with a thin cover glass and rotated between crossed nicols until it extinguishes. The analyzer should be removed and the tube of the microscope raised to see if the index of the crystal is the same as that of the liquid. Substitute liquids until the indices are the same. If the crystal is moved the analyzer should be replaced and the crystal turned to the position of extinction. To determine the other index of refraction, the crystal must be turned exactly 90° from its first position of extinction and the procedure repeated.

Refractive Index of Biaxial Crystals.—The three indices of biaxial crystals are designated by the Greek letters α, β, γ, and can be measured with some degree of accuracy by the immersion method if the fragments lie on their cleavage planes. A particle should be taken that shows strong birefringence. In judging this both color and thickness should be considered. The determination of α and γ is carried out as described for uniaxial crystals. A number of crystals should be measured. Some will give the lowest refractive index, α, and some will give γ, the highest. The intermediate index, β, lies between these values, and can be measured on a grain that shows little birefrigence. Such a grain may be considered normal to the optic axis. If only one index is to be measured β should be chosen. The grains can be turned over in the different media[1] by pushing the cover glass very slightly, and platy fragments like the micas can be determined by turning the plates on edge in a viscous liquid.

[1]Esper S. Larsen, Microscopic Determination of Nonopaque Minerals, Bulletin 679, Dept. of Interior, 1921.

Refractive Index Tables for Liquids

	Temperature Centigrade.	η.	Investigator.
Hydrochloric Acid	10°	1.254	Bleekrode
Ammonia (liquid) d .615	16.5°	1.325	Bleekrode
Hydrobromic Acid	10°	1.325	Bleekrode
Cyanogen (liquid)	18°	1.327	Bleekrode
Methyl alcohol	20°	1.329	Landolt
Acetaldehyde	20°	1.3316	Landolt
Water	20°	1.3329	
Dimethylamine	17°	1.350	Bleekrode
Ethyl ether	22°	1.351	Cheneveau
Triphenyl amine	16°	1.353	Bleekrode
Methyl chloride	0°	1.353	Chappuis
Ethyl formate	20°	1.358	Landolt
Pentane	15.7°	1.358	Landolt
Ethylene formate	20°	1.358	Landolt
Acetone	20°	1.359	Hubbard
Ethyl alcohol	20°	1.361	Rudolphi
Methyl acetate	14.8°	1.3632	Prytz
Ethyl carbylamine	24°	1.3659	Gladstone
Chlorine (liquid)	14°	1.367	Bleekrode
Formic acid	20°	1.371	Homfray
Acetic Acid	20°	1.372	Eisenhohr
Butyl aldehyde (iso)	20°	1.373	Brühl
Ethyl Acetate	16.4°	1.374	Fery
Hexane	20°	1.3754	Brühl
Propyl alcohol (iso)	20°	1.377	Brühl
Butyl aldehyde (normal)	20°	1.384	Brühl
Hydrogen Sulphide	18.5°	1.384	Bleekrode
Ethyl nitrate	21.5°	1.38484	Brühl
Ethyl carbonate	20°	1.38528	Brühl
Propyl alcohol (primary)	18.1°	1.386	Schütt
Di-ethylamine	17.6°	1.3873	Brühl
Acetic anhydride	20°	1.390	Landolt
Butyric acid		1.3922	
Acetyl chloride	20°	1.38976	Brühl
Hexylene	23.3°	1.3945	Brühl

	Temperature Centigrade.	η.	Investigator.
Propionic acid	0°	1.395	Korten
Butyl alcohol (iso)	19.6	1.396	Brühl
Butyl alcohol (normal)	20°	1.399	Brühl
Acrolein	20°	1.39975	Brühl
Valerianic acid	20°	1.4008	
Butyl nitrate	23.2°	1.401	Brühl
Amyl acetate	20°	1.402	Landolt
Ethyl sulphate	16.1°	1.4021	Nasini
Isoprene	18°	1.4041	Gladstone
Paraldehyde	20°	1.405	Brühl
Caproic acid		1.4055	
Amyl alcohol (primary)	20°	1.407	Brühl
Amyl alcohol (prim. norm.)	17.8°	1.408	Landolt
Amyl chloride	18.2°	1.4097	Jahn
Ethyl oxalate	20°	1.41043	Brühl
Decane	14.9°	1.4108	Landolt
Silicon tetrachloride	22.9°	1.412	Abati
Allyl alcohol	20°	1.41345	Brühl
Allyl Chloride	20°	1.41538	Brühl
Boron trichloride	5.7°	1.419	Ghira
Allyl amine	21.8°	1.41943	Brühl
Ethyl sulphate	11°	1.4198	Nasini
Sulphuric acid	15°	1.420	Veley
Glycol	20°	1.425	Landolt
Oenanthylic Acid	20°	1.426	Brühl
Ethylidine chloride	0°	1.4288	Weegmann
Ethyl mercaptan	20°	1.43055	Nasini
Ethylene glycol	22.5°	1.4306	Gladstone
Methyl amine	17.5°	1.432	Bleekrode
Ethyl bromide	8°	1.4320	Gladstone
Paraffine	38.3°	1.4329	Eykman
Hydroxylamine	23.5°	1.440	Brühl
Lactic acid	20°	1.441	Landolt
Formamide	22.7°	1.445	Brühl
Chloroform	20°	1.446	Lorenz
Ethylene chloride	17°	1.4466	Jahn

	Temperature Centigrade	η.	Investigator.
Acetyl-acetone	15.5°	1.449	Perkin
Piperidine	18.7°	1.453	Brühl
Chloral	20°	1.456	Brühl
Menthol	22°	1.460	Masson
Oleic Acid	17.8°	1.460	Eykman
Carbon tetrachloride	20°	1.4607	Haagen
Ethyl thiocyanate	22.9°	1.46533	Nasini
Allyl bromide	20°	1.46545	Brühl
Hydriodic acid	16.5°	1.466	Bleekrode
Hydrazine	22.3°	1.470	Brühl
Glycerine	20°	1.474	Damien
Nitroglycerine	18.6°	1.482	Gladstone
Allyl sulphide	26.8°	1.48770	Nasini
Ethyl benzol	14.5°	1.4994	Landolt
Toluene	20°	1.495	Brühl
Amyl Iodide	14°	1.4960	Gladstone
Xylene (meta)	20°	1.496	Brühl
Ethyl benzene	20°	1.496	Brühl
Xylene (para)	14.7°	1.498	Landolt
Benzene	20°	1.501	Brühl
Xylene (ortho)	21.6°	1.505	Brühl
Ethyl benzoate	20°	1.5057	Hoeck
Pyridine	21°	1.509	Brühl
Methyl benzoate	20°	1.51158	Landolt
Ethyl iodide	20°	1.51203	Lorenz
Anisol	21.8°	1.515	Nasini
Thymol	24.4°	1.519	Nasini
Phosphorous trichloride	15.4°	1.520	Nasini
Ethylidene bromide	0°	1.52455	Weegmann
Benzonitrile	25.5°	1.526	Brühl
Chlorobenzine	15°	1.526	Jahn
Furfurol	20°	1.526	Brühl
Allyl mustard oil	20°	1.5266	Berliner
Cuminol	26.0°	1.527	"Jones"
Nicotine	18.8°	1.529	Brühl
Thiophene	18.5°	1.530	Brühl

	Temperature Centigrade.	η.	Investigator.
Boron tribromide	6.3°	1.536	Ghira
Benzyl alcohol	20°	1.539	Brühl
Benzyl chloride	15.4°	1.5415	Brühl
Benzoldehyde	26.0°	1.542	"Jones"
Acetylene dibromide	20°	1.5428	Gladstone
Benzylamine	19.5°	1.544	Brühl
Ethylene bromide	10.5°	1.5446	Gladstone
Phenol	30°	1.550	Landolt
Toluidine (para)	20°	1.553	Brühl
Nitrobenzene	20°	1.553	Brühl
Benzoyl chloride	20°	1.55369	Brühl
Brom-ethylene (Di)	0°	1.556	Weegmann
Brom-benzene	20°	1.560	Brühl
Anethol	11.5°	1.5624	Eykman
Salicylic acid	20°	1.565	Landolt
Silicon tetrabromide	23.5°	1.563	Abati
Toluidine (meta)	20°	1.571	Brühl
Toluidine (ortho)	20°	1.573	Brühl
Triphenylmethane	99°	1.578	Perkin
Naphthalene	98.4°	1.582	Nasini
Aniline	20°	1.586	Brühl
Antimony pentachloride	17.5°	1.587	Gladstone
Brom-ethylene (tri)	20°	1.589	Jahn
Phenylhydrazine	20.3°	1.608	Brühl
Naphthol (alpha)	98.7°	1.62067	Nasini
Brom-aniline (meta)	20.4°	1.626	Brühl
Iodobenzene	8°	1.627	Perkin
Carbon disulphide	18°	1.629	Brühl
Bromine	20°	1.654	Riviere
Brom-naphthalene	20°	1.658	Brühl
Iodomethane (di)	25°	1.737	Perkin
Sulphur	130°	1.890	Becquerel

Wright's Series[1]

(Bulletin 158, Carnegie Institute)

Mixtures of petroleum and turpentine	1.450—1.475
Turpentine and ethylene bromide	1.480—1.535
Clove oil and α-monobromnapthalene	1.540—1.635
Petroleum and α-monobromnapthalene	1.475—1.650
α-monobromnapthalene and methylene iodide	1.650—1.740
Sulphur dissolved in methylene iodide	1.740—1.790
Methylene iodide and arsenic trisulphide	1.740—2.280

The above mixtures can be made from the formula of Schroeder van der Kolk,[2] in which n is the refractive index

$$n_1V_1 + n_2V_2 = n(V_1 + V_2)$$

of the mixture, V_1 and V_2 the volumes of the two liquids, n_1 and n_2 their respective refractive indices.

Laboratory Exercises for Studying Crystalline Substances

1. Separate the 150 wooden crystal models (secured from Ward Natural Science, Rochester, N. Y.) into six groups according to their crystal system. Locate the crystallographic axes and planes of symmetry.
2. Select 5 crystals having two or more forms. Name the forms appearing and determine the Weiss and Miller indices.
3. Study the behavior of fragments of sodium chloride, beryl and copper sulphate between crossed nicols. Which give parallel extinction and which oblique?
4. Select three compounds of known refractive index. Determine their refractive index and see how accurate are your results.
5. Check the color order of the following and determine the approximate birefringence:

   Potassium chloride, black; apatite, gray or white; talc, bright B; calcite, high order.

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[1]Recommended by Cornell Laboratories.
[2]Mikroskopische Krystallbestimmung, Weisbaden, 1898, page 13.

Study the behavior of the following compounds with polarized light, selenite plate, mica plate, and quartz wedge. Try out their crystallization in water and in the presence of some colloid such as gum arabic. Have they greater or less refractive index than glycerine?

ISOMETRIC SYSTEM. Sodium chloride; barium nitrate; potassium alum.

TETRAGONAL SYSTEM. Mercuric cyanide; strychnine sulphate; potassium cobaltinitrite; Magnesium ammonium arsenate; potassium di-hydrogen phosphate.

HEXAGONAL SYSTEM. Sodium nitrate; cadmium iodide; sodium sulphite.

ORTHORHOMBIC SYSTEM. Potassium sulphate; ammonium sulphate; potassium nitrate.

MONOCLINIC SYSTEM. Potassium chlorate; barium chloride; potassium carbonate.

TRICLINIC SYSTEM. Potassium bichromate; copper sulphate.

Observe the pleochroic behavior of copper acetate and silver bichromate.

Measure the extinction angle on ammonium sulphate; barium chloride; copper sulphate; silver acetate.

CHAPTER III

Chemical Microscopy

Value of Analytical Microscopy.—The relative values of the old methods of qualitative analysis and the modern microscopic methods can be better understood from the following advantages which have been well established:

1. The time required for analysis is shorter than the old methods.
2. It is just as accurate and can be made considerably more so.
3. It is cleaner, the student can be more comfortable and will develop neat habits.
4. It is very much wider in its application. It can do everything that old qualitative analysis can do and in addition many other things.
5. The initial cost is approximately the only cost.
6. The use of such minute quantities of materials makes possible a class study of the rarer elements—a thing impossible under the old system.
7. The complete laboratory can be converted into a field laboratory at a moment's notice.
8. The student learns in the theory of microscopy, not only such things as equilibrium, colloids, mass action, etc., but also crystallography, mineralogy, the principles of light, photography, and the chemical behavior of not only the common but the rarer elements as well. He learns also some very practical biology.

Equipment for Elementary Work. — Almost all of the dry reagents needed are found in the standard *Chamot reagent block*.[1] This block contains sixty small glass vials with ground glass stoppers. A chart is furnished with the block which enables one to readily find the desired chemical.

[1] These can be furnished by the Will Corporation, Rochester, N. Y.

Laboratory Chemical Microscopy—Cornell University

Key to Reagents in Reagent Blocks

	1	2	3	4	5	6	7	8	9	10	11	12	
A	Silver Nitrate	Stannic Chloride	Potassium Sulpho-cyanate	Calcium Acetate	Potassium Sulphate	Sodium Sulphate	Sodium Bicarbonate	Potassium Chlorate	Potassium Bichromate	Oxalic Acid	Litmus Silk	Ammonium Fluoride	A
B	Chloro-platinic Acid	Perchloric Acid	Dimethyl Glyoxime	Cobalt Acetate	Mercurous Nitrate	Mercuric Bromide	Ammonium Carbonate	Potassium Persulphate	Potassium Chromate	Potassium Oxalate (Acid)	Congo Red Silk	Cesium Sulphate	B
C	Barium Chloride	Silicon Dioxide	Lead Nitrate	Copper Acetate	Potassium Nitrite	Lead Acetate	Sodium Carbonate	Ammonium Chloride	Potassium Ferro-cyanide	Ferric Chloride	Morphine Sulphate	Nitron Sulphate	C
D	Cesium Chloride	Rubidium Chloride	Sodium Bismuthate	Zinc Acetate	Sodium Thio-sulphate	Arsenic Acid	Potassium Carbonate	Citric Acid	Potassium Perman-ganate	Magnesium Chloride	Tumeric Filaments	Magnesium	D
E	Potassium Mercuric Sulpho-cyanate	Potassium Iodide	Sodium Hydroxide	Sodium Acetate	Ammonium Acetate	Uranyl Acetate	Bismuth Sulphate	Sodium Phosphate (Secondary)	Ammonium Molybdate	Starch	Zinc Sulphide Wool	Zinc	E
	1	2	3	4	5	6	7	8	9	10	11	12	

Arsenic Acid....6D
Ammonium Acetate....5E
Carbonate....7B
Chloride....8C
Fluoride....12A
Molybdate....9E
Barium Chloride....1C
Bismuth Sulphate....7E
Calcium Acetate....4A
Cesium Chloride....1D
Sulphate....12B
Chloroplatinic Acid....1B

Citric Acid....8D
Cobalt Acetate....4B
Congo Red Silk....11B
Copper Acetate....4C
Dimethyl Glyoxime....3B
Ferric Chloride....10C
Lead Acetate....6C
Nitrate....3C
Litmus Silk....11A
Magnesium Chloride....10D
Metal....12D
Mercuric Bromide....6B

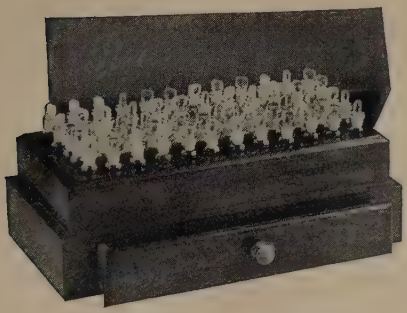
Mercurous Nitrate....5B
Morphine Sulphate....11C
Nitron Sulphate....12C
Oxalic Acid....10A
Perchloric Acid....2B
Potassium Bichromate....9A
Carbonate....7D
Chlorate....8A
Chromate....9B
Ferrocyanide....9C
Iodide....2E
Mer. Sulphocyanate....1E

Potassium Nitrite....5C
Oxalate (Acid)....10B
Permanganate....9D
Persulphate....8B
Sulphate....5A
Sulphocyanate....3A
Rubidium Chloride....2D
Silicon Dioxide....2C
Silver Nitrate....1A
Sodium Acetate....4E
Bicarbonate....7A
Bismuthate....3D

Sodium Carbonate....7C
Hydroxide....3E
Phosphate....8E
Sulphate....6A
Thiosulphate....5D
Stannic Chloride....2A
Starch....10E
Turmeric Filaments....11D
Uranyl Acetate....6E
Zinc Acetate....4D
Metal....12E
Sulphide Wool....11E

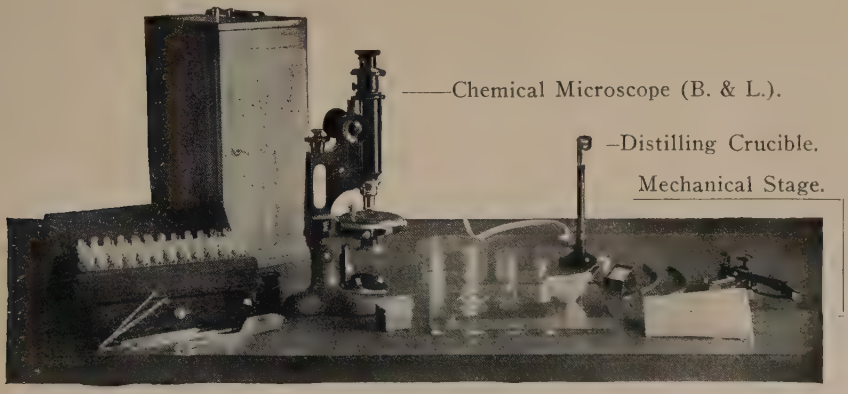
CAUTION.—Never remove from the block more than ONE vial at a time. Use special care to avoid mixing stoppers and contaminating reagents.

To describe in detail all of the apparatus and equipment possible to use in microscopy is not the purpose of this book.[1] There should be available as a *minimum* equipment apparatus for polarized light, opaque and dark field illumi-



Chamot Reagent Block with Drawer.
Fig. 13.

Chamot Reagent Block.
Fig. 12.



Miscellaneous Equipment (Supplied by Will Corp., Rochester, N. Y.).
Fig. 14.

nation, determination of melting points, micrometer oculars, a quartz wedge, mica plate and also a selenite. A "daylight lamp," and an arc lamp for photography are both essential, as are the previously described vials and chemicals.

[1]For such description see Chamot's Elementary Microscopy, John Wiley & Sons.

The following additional equipment will be found very convenient for special problems:

Mechanical stage	Centrifuge
Distilling tubes	Sieves
Platinum spatula	Filters
Forceps with platinum tip	Condensing lens
Small quartz evaporator	Burner with crucible holder
Agate mortar	

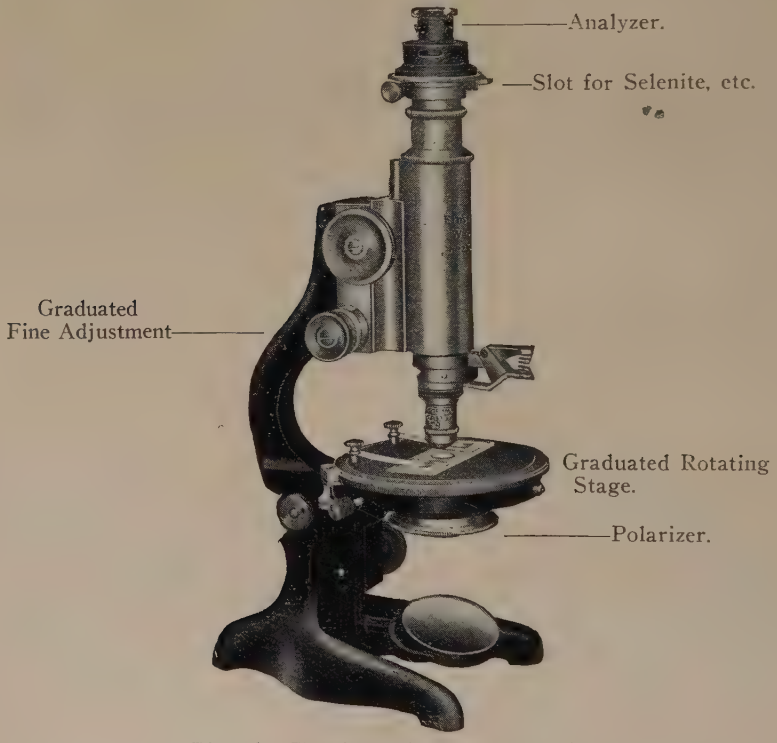


Fig. 15. Chemical Microscope (Leitz).

Liquid Reagents.—These are kept in small dropping bottles and can be purchased from supply houses cheaply. Special containers are available for hydrofluoric acid. The use of this reagent can be often avoided by substituting ammonium silicofluoride and a drop of hydrochloric acid which react with the formation of HF.

The following liquid reagents are essential:

Dilute 1:4	*Conc.*
HCl	H_2SO_4
H_2SO_4	HCl
HNO_3	NH_4OH
NH_4OH	
H_2O	
$2KCNS.Hg(CNS)_2$	
$HC_2H_3O_2$	

Polarizing Tubes.—A Bates[1] polarizing tube placed in the draw tube of the chemical microscope converts the instrument into a simple polariscope. It is difficult however to obtain very accurate readings on account of the small circumference of the graduated circle of the analyzer. Parallel yellow light should be used and the average of a number of readings taken. Before the filled tube is inserted in the microscope care should be used to insure proper crossing of the nicol prisms, so that when the tube is inserted and the nicols rotated to maximum darkness again the readings showing the degrees of rotation can be relied upon. To secure more accurate reading of the end point a dark cloth, thrown over the head of the observer and the top of the instrument, is a great convenience.

If "X" is the angle of rotation, "g" the number of grams of the substance in 100 c.c. of solution, and "L" the length of the polarizing tube in decimeters, the equation for specific rotation would be

$$\text{Specific Rotation} = \frac{100\,X}{Lg}$$

The specific rotation is usually known. After "X" has been measured the concentration can be determined by solving the equation for "g."

Burner.—The most useful burner for general purposes is the Bunsen burner with a pilot flame. The gradations in heat intensity can then be available over a very wide

[1] Bates tubes can be purchased from Bausch & Lomb, Rochester, N. Y.

range. The small pilot flame is the one most often used, as very little heat is usually required.

Chilling Plate.—It is often very important to suddenly chill the glass slide upon which the concentration is taking place so that the preparation will not go completely to dryness. This can be accomplished by placing the warm slide down against the surface of a piece of plate glass for a moment. The heat is very rapidly conducted away.

Varnished Slides.—If reactions are to be undertaken involving the use of fluorides it is essential that varnished slides and cover glasses be employed. If not the silica from the glass would react and give a test which might not be desirable. The cover glass must be used to protect the lens of the objective from the destructive action of the acid.

Hot Stages.—These are very convenient when it is desired to keep the preparation at a temperature greater than that of the room. They are essential when a melting point determination is to be made. They can be found in the catalog of almost any supply house.

Camera Lucidas.—When it is desired to make a permanent record of the field under observation and a photographic outfit is not available a small Abbe[1] drawing camera will be found convenient. It is attached to the tube above the ocular and is so constructed that both the object and the drawing paper can be seen at the same time. Rays from the drawing paper strike the surface of the mirror and are reflected into a cube of glass located just above the ocular. The cube has been cut diagonally and before being cemented together has had one surface silvered. A small hole has been left in the silvered surface so that light from the preparation can enter the eye. The light rays from the drawing paper, reflected into the cube by the large mirror, strike the silvered surface and are again reflected, reaching the eye simultaneously with those from the object. With such an instrument it is possible to trace delicate structure very accurately.

[1] Manufactured by Bausch & Lomb.

It is important that the small opening in the silvered surface of the glass cube be exactly at the eyepoint in order to prevent the loss of considerable light. For this reason the large Abbe[2] drawing camera is more convenient than the smaller type.

The "Drawing Eyepiece" manufactured by E. Leitz[3] has a negative eyepiece with a reflecting prism inserted above the eye lens. By extending the prism to the optic axis of the ocular the light rays from the drawing are twice reflected and enter the eye of the observer simultaneously with the image rays.

Microspectroscopes.—The microspectroscopes upon the market at present cannot compete with the high-grade spectroscopes when accuracy is desired. That manufactured by W. & H. Seibert, Wetzlar, Germany, is considered one of the best. Unfortunately the cost of such attachments is excessive when the value of the results obtained is considered. More complete descriptions of such instruments can be obtained from the manufacturers and directions for use found also in Chamot's *Elementary Chemical Microscopy*.

LABORATORY TECHNIQUE

Sampling Rods.—It is important that the beginner become familiar very early with the general procedure to follow, and he should endeavor to develop considerable technique in carrying out the fundamental operations such as decantation, sublimation, filtration, etc.

Chemicals are removed from the reagent vials by means of a solid glass rod drawn out to a tapering point. The rod should be small enough to enter the mouth of the vial easily, and should be carefully wiped after use. Failure to do so results in early contamination of the reagents.

The rod is also used for transferring drops of liquids from the pipettes to the glass slides. The pipette containing the desired reagent is removed from the dropping bottle

[2]Manufactured by Spencer Lens Co.
[3]E. Leitz, Wetzlar, Germany.

and a drop of the liquid is placed about half way up on the glass rod and allowed to slide down to the point from which it is removed by touching the slide. In this way the size of the drop can be controlled and the point of the pipette does not come in contact with the test drop, thus eliminating contamination. *Drops should be small and spherical.*

Precipitation.—On the glass slide place a small round drop of a solution containing a calcium compound. Add to this drop a trace of dilute sulphuric acid. If precipitation is not immediate warm gently and then examine the margin of the drop for needles of calcium sulphate ($CaSO_4.2H_2O$).

If precipitation occurs only in the presence of an excess of one of the reagents that reagent is added in the form of a tiny fragment.

If precipitation is immediate the crystals may be too small for practical study. They must be recrystallized from hot water, acid, ammonium hydroxide or some medium from which the crystallization will be slower.

Decantation.—Place a drop of distilled water upon an object slide. Dissolve in this a *tiny fragment* of silver nitrate which can be transferred from its vial by means of the sampling rod. When the fragment is dissolved wipe the rod carefully and then place adjacent to the silver nitrate solution a small drop of dilute HCl. With the point of the sampling rod lead the two drops together. The precipitation of silver chloride will be immediate. Place the point of the sampling rod on the edge of the supernatant liquid and carefully lead the liquid away from the precipitate which should cling to the slide. Cut the connecting film between the precipitate and the decanted liquid by means of a narrow strip of filter paper.

The precipitate can be *washed* by adding a drop of water and decanting as before.

Sublimation.—Place a small amount of benzoic acid upon the corner of a thin object slide. Hold the middle of the slide over the pilot flame of the Bunsen burner

and allow the temperature to gradually increase. When sublimation begins hold over the preparation another slide upon whose upper surface a drop of water rests. The slides should be about 3 millimeters apart and the water should be so placed on the upper slide that the sublimate will condense on the under surface of the upper slide directly beneath the water. To prevent the preparation being blown away it is wise to moisten the material and then dry it thoroughly. The material should not be spread on so thick that there will be lack of uniformity in heating. *Examine the sublimate with the microscope.*

Make a mixture of benzoic acid and phthallic anhydride. Fractionally sublime the preparation by moving the "condenser slide" every few seconds so that at least six different sublimates are formed on the same slide. Examine each deposit with the microscope and notice where the greatest concentration of each component is to be found.

If the substance to be sublimed is in a solution, it is best to repeatedly evaporate several drops at the same place on the slide until sufficient solid material has been accumulated to proceed as in the case of solids. Sublimation is often practiced in studying organic compounds.

Filtration.—Method of Streng. The slide bearing the preparation to be filtered is placed on the bottom of an upturned box. The box should slightly incline. A strip of filter paper 2 mm. broad is touched to the turbid drop at one end. The other end of the paper hangs down and touches a clean slide placed below to receive the filtered liquid. Precipitate silver chloride from a solution of silver nitrate by means of dilute hydrochloric acid and filter. About five milligrams of water will be retained in the filter paper. This must be considered when deciding upon the size of the drop to be filtered.

Method of Behrens. Precipitate a small amount of silver chloride on a object glass as before. Place near the drop a small square of filter paper with one corner touching the liquid. Press down upon this filter paper the end

of a glass tube which should be about six millimeters long with a 1.5 millimeter bore, one end of which should be ground smooth and the other end rounded so that it can be inserted in a small rubber tube fitted with a short glass rod for a mouthpiece. Suction is applied at the mouthpiece when the paper becomes wet and the filtered liquid is drawn into the tube. The liquid can be forced from the tube by holding it over another slide and applying pressure on the rubber tube, or removed if necessary by blowing gently at the mouthpiece.

Distillation.—When such volatile substances as ammonia are to be distilled the apparatus recommended by Chamot is very convenient. A small porcelain crucible (a glass one can be made from a test tube if necessary) is placed in the wire holder above the Bunsen burner (Fig. 14). A small amount of ammonium sulphate is introduced in the crucible and then a drop of sodium hydroxide added. An object glass carrying a hanging drop of dilute hydrochloric acid on the under side is placed over the crucible. The preparation is then warmed gently over the pilot flame and the escaping ammonia fixed in the hanging drop as ammonium chloride. This drop may be tested for ammonia with H_2PtCl_6. Bright yellow octahedra will be present.

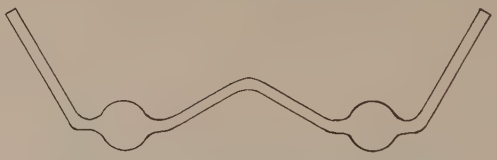


Fig. 15½. Distilling Apparatus (Behrens).

Behrens recommends for very volatile liquids an apparatus made by blowing two bulbs in a small glass tubing. (Fig. 15½.)

To charge the miniature still one end of the small tubing is fused. After cooling the open end is introduced into a drop of the liquid and the upper bulb is warmed to drive out air. As the apparatus cools the liquid is drawn up into the bulb.

To carry out the distillation after the sample has been introduced, open the *closed* end, seal the open end and warm gently. This will drive the liquid over into the other bulb which can be kept cool by drops of ice water. The distillate can be removed by opening the sealed end and blowing gently.

Impregnated Fibres.—*Litmus silk* is used to detect the presence of acids or alkalies. The raw silk is first boiled in a dilute soap solution, rinsed and then for two hours is treated with a 10% sodium hydroxide solution. It is then rinsed again and dyed with a 10% solution of litmus to which has been added a few drops (3 or 4) of 1:4 sulphuric acid.[1] Heating should continue until the solution is syrupy. The silk is then removed, rinsed and neutralized with sodium hydroxide, the excess of which is removed by thoroughly washing.

Tumeric silk is made from viscose. The fibers are boiled in a 50% alcoholic, alkaline solution of tumeric made by digesting 20 grams of the ground root in 50 c.c. of boiling alcohol, adding an equal volume of water to the filtered solution made alkaline by the addition of a drop of 10% sodium hydroxide.[2] When the fibers have been boiled in this solution until a syrupy condition exists, they are removed, dipped in 95% alcohol, pressed between filter papers, washed in dilute sulphuric acid, rinsed thoroughly in water and dried. If the silk is not a bright golden yellow it should be treated with alcohol again and washed in water.

Zinc sulphide wool is made from wool swollen by a 10-hour soaking in 1% solution of sodium hydroxide. After being thoroughly washed it is dipped repeatedly first in a solution of 10% zinc acetate and then a solution of 10% sodium sulphide. After about six alternate dippings the fibers are washed and then dried. The wool should be defatted by a mixture of alcohol and ether.

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[1]Chamot & Cole: J. Ind. Eng. Chem., IX (1917) 969.
[2]Chamot & Cole: J. Ind. Eng. Chem., X (1918) 48.

Laboratory Exercises in Absorption[1]

1. Into a *very dilute* drop of hydrochloric acid on a glass object slide place a blue litmus fiber (silk). The silk fiber should extend into the drop and should have sufficient length so that at least two-thirds of the fiber be outside the drop. The liquid will gradually be absorbed into the thread. Examine the thread with the microscope.
2. Prepare a red or yellow silk fiber by placing a thread of raw silk in a drop of gold chloride, and evaporating. On this colored fiber place a drop of $SnCl_2$ and a trace of tannic acid. The fiber becomes purple with colloidal gold. (Chamot.)
3. To a drop of solution containing potassium chloride add a small amount of perchloric acid. Almost immediately characteristic crystals of potassium perchlorate will separate. These colorless crystals can be stained a pink in the presence of a permanganate solution.
4. To a solution containing potassium iodide add a few grains of starch and a trace of dilute sulphuric acid. The starch should be stained blue from absorbed iodine.
5. To a drop of gold chloride add a small fragment of thallous nitrate. Long yellow needles are formed almost immediately. It is very probable that this is not strictly absorption but a definite compound.
6. Place a fiber of zinc sulphide wool in a drop of copper sulphate that has been slightly acidified. After staining has taken place examine the thread with the microscope.
7. Repeat the experiment, using a solution of antimony trichloride instead of copper. Then try solutions containing tin, cadmium, silver, or arsenic.

Metallic Deposits.—Every element in the electrochemical series should be able to replace any one below it in solution. In many instances the form of the crystallizing metal is quite characteristic and also aids the investigator in either

[1]Impregnated fibers are due to Emich and Donau. They have been further improved by Chamot & Cole.

degree of accuracy just what elements are actually present. removing objectionable elements or determining with some The electrochemical series of Wilsmore-Ostwald is convenient.

Laboratory Exercise

Mg
Al
Mn
Zn
Cd
Fe
Tl
Co
Ni
Sn
Pb
(H)
Cu
As
Bi
Sb
Hg
Ag
Pd
Pt
Au

To a solution of lead nitrate add a tiny fragment of magnesium metal and examine the branching crystals under the microscope.

To a solution of copper sulphate add a small fragment of zinc. Before examining the preparation under the microscope add a trace of acid.

To a solution of silver nitrate add a bright fragment of copper.

To a solution containing mercury add a bright fragment of copper.

To a solution containing zinc add a fragment of metallic tin. Notice that there is no deposit formed on tin. Why?

Double and Triple Salts.—The student is impressed with the number and importance of double, complex and triple salts used in microchemical analysis. It is important to remember that in the building of such salts the alkali metals are often used and that the solubility of such compounds is lessened when an alkali metal of higher atomic weight is employed. Thallium (valence 1) acts as an alkali metal in many compounds and forms the least soluble salt of such a series.

Advantage is taken of this fact to increase the delicacy of many reactions. Platinum is usually detected as potassium chloroplatinate but the use of rubidium chloride instead of potassium makes the test far more delicate, cesium chloride is still more efficient and thallous chloroplatinate is even less soluble.

On a glass object slide place three drops of chloroplatinic acid a short distance apart. To one drop add a drop of potassium chloride, to the second add a drop of rubidium

chloride, to the third add a drop of cesium chloride. Examine each drop under the microscope and note the relative size of the crystals and their rapidity of formation.

Thin Films.—It sometimes is necessary to have a high concentration of one of the reacting substances present in order to secure good crystal formation. This condition can in some cases be brought about by addition of solid reagents to the test drop. It is often necessary to prepare a thin film of the substance to be tested by carefully evaporating the unknown solution over the pilot flame so that after evaporation has taken place a uniform film remains. Place near this film a drop of the precipitating reagent and with the point of the sampling rod draw a narrow channel of the reagent across the film. Crystallization should start on the edges of the channel.

Prepare a thin film of sodium acetate. Lead across this film a solution of uranyl acetate. Note the formation of yellow tetrahedra ($NaC_2H_3O_2 . UO_2(C_2H_3O_2)_2$ along the edges of the channel. (See page 141.)

Melting Point Determination. — For low melting point determinations a hot[1] stage can be made from a glass box such as is used in the spectroscope examination of liquids. The open end is closed with a three-holed rubber stopper. The central hole is for the insertion of Anschutz thermometers and the outer ones for the intake and outlet tubes through which the hot liquid circulates from a small copper coil heated by means of a Bunsen burner.

For temperatures higher than 150° an electrically[2] heated hot stage must be employed, such as is described by Chamot, Cram and others, and for very high melting points micropyrometers[3] must be used.

If only the approximate melting point is desired it can be obtained by comparison. Replace the rotating stage, if

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[1]Chamot & Albrech, Unpublished Paper Read at the Cornell Section of Am. Chem. Soc., May, 1906.

[2]Chamot, Elementary Chem. Microscopy, 1921, page 222.
Cram, J. Am. Chem. Soc., 34, 1912, 954.
Cottrell, J. Am. Chem. Soc., 34 (1912), 1328.

[3]Burgess, A Micropyrometer. Cir. 198, U. S. Bureau of Standards.

necessary, with an asbestos disk carrying a central hole. Make a tiny gas jet out of a piece of drawn out tubing and place it in a cork which will fit snugly in the substage ring. This will permit the raising or lowering of the flame by means of the screw.

If two fragments of the same size placed closely together on a glass slide over this tiny flame melt simultaneously they have melting points approximately the same. Known substances can be substituted beside the unknown until one is found which does melt at the same time, or two found between which the unknown has its melting point. For this work a table of known melting points is convenient.

TABLE OF MELTING POINTS

M. P. C°	
10	Ethylenediamine
12	Paraldehyde
13	Pyruvic acid
14	Oleic acid
15	Amino p-Xylene
16	Acetic acid
17	Methyl myristate
18	Methyl succinate
20	Tetrahydroquinoline
21	Anethole
24	α-Bromopropionic acid
25	tert-Butyl alcohol
26	3-Bromo 4-Aminotoluene
27	Methyl palmitate
28	Guaiacol
29	Bornyl acetate
30	Capric acid
31	o-Bromoaniline
33	Levulinic acid
34	α-Benzoldoxime
35	Pinacone
36	Methyl cinnamate
37	Piperonal
38	Methyl stearate
39	Myristyl alcohol
40	α, γ-Dichloroacetone
41	Cyanamide
42	Phenol
43	α-Hydroxybutyric acid
44	Bromal alcoholate
45	p-Toluidine
46	Formanilide
47	α-Acetaldoxime
48	Methyl tartrate
49	1, 2, 4-Xylidine
50	Bromacetic acid
51	Procaine base
52	Methyl carbamate
53	Bromal hydrate
54	Methyl oxalate
55	Chloral alcoholate
56	Pinacone hydrate
57	Trichloracetic acid
58	Orcinol (hydrate)
59	Chloral hydrate
60	Acetoxime
61	Trichlorolactonitrile
62	Tetramethyl ammonium hydroxide
62	Palmitic acid
63	Chloroacetic acid
64	α, β-Dibromopropionic acid
65	1, 2, 4-Xylenol
66	Cyanoacetic acid
67	s-Trichlorophenol
68	Pseudocumidine

M. P. C°	
69	Stearic acid
70	Dibenzylaniline
71	o-Nitroaniline
72	α-Crotonic acid
73	p-Dimethylamino benzoldehyde
74	Ethyl phenylcinchoninate
75	8-Hydroxyquinoline
76	Phenylacetic acid
77	s-Trichloroaniline
78	Glycolic acid
79	Methyl citrate
80	2, 4-Diaminophenol
81	2-Hydroxy—1-Napthylaldehyde
82	β-Iodopropionic acid
83	Benzoyl carbinol
84	Iodoacetic acid
85	Sulphoacetic acid
86	Diglycolide
88	Benzenesulfonyl benzylamine
89	Ethyl p-Aminobenzoate
90	n-Butyranilide
91	Tribenzylamine
92	p-Toluenesulfonic acid
93	m-Nitrophenol
94	α-Napthol
95	Laevulose
96	Phenoxyacetic acid
97	Glutaric acid
98	l-Cocaine
99	2-Amino—5-Azotoluene
100	Peracetic acid
101	Oxalic acid (hydrate)
102	Methyl acetanilide
103	Benzoyl peroxide
104	Catechol
105	Pimelic acid
106	p-Aminoacetophenone
107	Acridine
108	Dehydracetic acid
109	α-Nitroso β-Napthol
110	Resorcinol

M. P. C°	
111	Ethylmalonic acid
112	Dibenzylidineacetone
114	m-Nitroaniline
115	Atropine
116	Benzoquinone
117	Benzylmalonic acid
118	9-Raffinose (anhydrous)
119	2, 4, 6-Trinitrobenzaldehyde
120	d-Camphoroxime
121	Benzoic acid
122	m-Aminophenol
123	Hydroquinone diacetate
124	Trichlorolactic acid
125	p-Aminoazobenzene
126	Phenylglycine
127	Benzidine
128	p-Diiodobenzene
129	Pinenehydrochloride
130	Maleic acid
131	Phthalic anhydride
132	d-Mannose
133	Pyrogallol
135	Acetylsalicylic acid
136	Picolinic acid
137	Benzoin
138	2, 6-Dinitroaniline
140	p-Phenylenediamine
141	Orthoform
142	m-Nitrobenzamide
144	5-l-Xylose
145	α-Triphenylguanidine
146	Glucose
147	Papavarine
148	Oxanilic acid
149	6-Nitroquinoline
150	Benzilic acid
151	4-Hydroxy m-Toluic acid
152	Adipic acid
153	Citric acid (anhydrous)
154	pp′-Dichloroazoxybenzene
155	l-Codeine
156	Benzaldehyde phenylhydrazone
157	Salicylic acid

M. P. C°	
158	m-Chlorobenzoic acid
159	Aceto α-Naphthylamine
160	l-Arabinose
161	Itaconic acid
162	p-Aminoacetanilide
163	p-Nitrodimethylaniline
164	6-Nitroquinaldine
165	Arbutin (glucoside)
166	d-Mannitol
167	Tribromo tert-Butyl alcohol
168	2, 4-Dinitro 6-Aminophenol
169	Hydroquinone
170	d-Galactose
171	Quinidine (dextro)
172	Phenylethylbarbituric acid
173	5-Amino o-Cresol
174	m-Aminobenzoic acid
175	Helicin (glucoside) ; quinine
176	Narcotine (laevo)
177	p-Toluic acid
178	Brucine (laevo)
179	Inulin
180	2, 4-Dinitroaniline
181	Methyl Red
182	Naphthalene tetrachloride
183	o-Iodobenzamide
184	p-Aminophenol
185-9	Succinic acid
186	p-Aminobenzoic acid
187	d-Camphoric acid
187	Hippuric acid
188	Oxalic acid (anhydrous)
190	Aconitic acid
191	Diacetyl m-Phenylenediamine
194	Acetylphenylglycine
196	m-Nitrocinnamic acid
199	2-Hydroxyquinoline
200	m-Hydroxybenzoic acid

M. P. C°	
201	Salicin
202	Phenanthraquinone
203	Lactose
204	3, 5-Dinitrobenzoic acid
205	Veratrine
206	p-Coumaric acid
207	Cinchonidine
210	Phenylcinchoninic acid
213	p-Hydroxybenzoic acid
214	p-Cyanobenzoic acid
216	Piperic acid
217	p-Iodobenzamide
218	Phloroglucinol
219	Phthalamide
226	Succinanilide
228-30	Nicotinic acid
229	Hexachlorobenzene
230	Quinolinic acid
233	Phthalimide
234	d & l-Asparagine
235	Caffeine
237	o-Nitrocinnamic acid
238	p-Nitrobenzoic acid
240	Glycogen
242	p-Chlorobenzoic acid
246	Nitroguanidine
250	Morphine
251	p-Bromobenzoic acid
259	p-Sulfobenzoic acid
261	Acenaphthoquinone
263	dl-Phenylalanine
265	Cinchonine (dextro)
268	Strychnine (laevo)
270	Theophyllin
274	Naphthalic acid
285	p-Nitrocinnamic acid
289	Alizarin
290	Fluorescein
300	Isophthalic acid
302	2-Aminoanthraquinone

PHOTOMICROGRAPHY

Illumination.—In making photomicrographs many things have to be considered, chief among which is the illumination. This can be best obtained from one of the standard arc lamps on the market. The automatic feed arc lamp is more satisfactory but expensive. The cheaper hand feed type has been used by the author and has given satisfaction. To use poor illumination is a waste of time and material.

It can be operated from any house circuit socket by interposing a rheostat to regulate the current. It is mounted upon a stand adjustable in height, can be tilted at any

Fig. 16. Arc Lamp.

angle, has a bull's-eye for condensing, a sliding tube for focussing, and a device which permits the carbons to be fed independently or simultaneously. With this type of lamp direct current is more satisfactory than the alternating.

A filament lamp containing a powerful bulb and a device for removing heat rays is now on the market and gives a steady light with both direct and alternating currents.

Light Filters.—These may be either dry or wet. The colored Wratten filter is a very satisfactory example of the dry type.

Wet filters for blue, green and red give about the following absorptions:

	Microns
Blue	.4500
Green	.5500
Red	.6500

The blue is made by mixing 23 parts of a 1 per cent solution of Victoria blue with nine parts of a 1 per cent solution of napthol-green. The mixture is diluted with 460 parts of water.

The green is made by mixing four parts of a 1 per cent solution of "rapid filter green" with four parts of a 1 per cent solution of "rapid filter K yellow." The whole is diluted with 460 parts of water.

The red is made by mixing 46 parts of a 1 per cent solution of rose Bengal with 46 parts of a 1 per cent solution of "rapid yellow filter K." The whole is then diluted with 460 parts of water.

For general purpose work the dry GREEN filter is most widely used.

THE MAGNIFICATION.— This is obtained from the objective, the eyepiece, and the length of projection. It is very important that the objective used be corrected for both spherical and chromatic aberration. For general purpose work the 16 or 8 mm. objectives are most used. They have considerable penetrating power and can therefore pick up images in different planes more readily than a higher power. A 10x or 25x eyepiece properly constructed can be used to increase the size of the image if desired. In some cases, however, it is essential that higher powered objectives be used. It must be remembered that any defect in the objective is greatly magnified by the eyepiece, and this in turn will be magnified in the projection on the plate. No matter how carefully you have selected the objective it will be worth little if the microscope is not equipped with a *carefully constructed fine adjustment.* A 10-inch extension of the camera is usually employed.

CONTRAST.— This is the result of using a powerful source of light and then filtering it through a suitable filter, such as the green, yellow or blue Wratten filters. If 8 mm. or 4 mm. objectives are used by lowering or raising the substage condenser until the sharpest outlines are observed greater contrast is obtained. Slow plates exposed over long

periods give better contrast than fast plates. The plates should be developed until black. If necessary prints can be made from these black plates by the use of daylight, rather than by artificial light. By observing these simple rules the writer has taken many pictures of transparent objects and gotten good results, even when the refractive index of the crystal and mother liquor were close.

Time of Exposure.— This will depend upon the intensity of the light and its distance from the microscope. It will also depend upon which side of the mirror is used, the height of the substage condenser and the magnification of the objective and its light-grasping power. If the preparation is stained this also will be a factor. In some cases it will be necessary to expose for twenty or more minutes. In others only a minute or two is necessary, sometimes less. After a few failures the beginner will learn to gauge the time correctly for each type of plate used.

Selection of Plates.— The illustrations for this book were made from standard Eastman lantern slides, but any standard plate would have done. It saves time to become familiar with the behavior of a certain brand, and you know better what to expect. These negatives can be used either for making prints or for projection work. One does not have to be as careful with slow plates as with fast ones.

Printing.— For thin negatives the glossy "F 4" brand of Azo paper gives fairly good results. For darker negatives the "F 2" variety can be used. Some workers prefer the Velox.

A suitable printing frame is not expensive. The negative is placed in the frame with the sensitive side up. The sensitive side of the printing paper is laid down on this and the back of the printing frame clamped on. If daylight is used the exposure in most cases should be very short. The time will depend upon the blackness of the negative. In the beginning some are always spoiled.

If the plate is not uniform in blackness the print will appear overexposed in some places and underexposed in others. This can be remedied by moving a piece of cardboard back and forth before the thin places while the print is being exposed. This cuts off some of the light from those spots.

After developing and fixing the prints should be thoroughly washed in running water for at least thirty minutes, and while still damp be placed on a ferrotype plate face down and a "squeegee roller" passed over them to press out the surplus water. When dry they will have a bright gloss. If they have a tendency to stick to the plate a solution of paraffene in benzene can be spread on the surface of the plate and when dry polished with a rag.

For special work the prints can be made on paper backed with linen.

Developers of Dry Plates.—There are a large number of formulae in the literature and an even larger number in the trade which work with considerable success. It would be useless to give them all here even if the writer were familiar with them. A good average is

Metol-hydroquinone.—Metol, ¾ gr.; hydroquinone, 3 gr.; sodium sulphite, 24 gr.; sodium carbonate, 36 gr.; potassium bromide, ¼ gr.; water, 1 oz.

Some of the other developers often used are

Pyro-soda.—Pyro, 2 gr.; sodium sulphite, 22 gr.; sodium carbonate cryst., 22 gr.; potassium bromide, ¼ gr.; water, 1 oz.

Hydroquinone, 2 gr.; soda sulphite, 6 gr.; sodium hydrate, 4 gr.; potassium bromide, ¼ gr.

Metol, 2 gr.; soda sulphite, 22 gr.; sodium carbonate cryst., 13 gr.; potassium bromide, ¾ gr.

Amidol, 2 gr.; sodium sulphite, 22 gr.; potassium bromide, 1 gr.

Development Factors. — The total time of development divided by the time it takes the first image to appear is known as the "factor" of the developer. Hydroquinone is a short "factor" developer and metol is a long. The former is from 4 to 5, while the latter requires 5 times as long. If it takes one-half minute for the image to first appear the plate should be developed for fifteen minutes if metol is used. Unless this is done the plate will be underdeveloped. The factor for amidol is from 7–10; for pyro it is from 4–7. The estimated factor for American pyro-soda developers is from 10–12.

Temperature Control.—Usually the speed of a reaction is accelerated by increasing and slowed down by decreasing the temperature. Warming the developer to about 90°F will greatly *accelerate* the development of underexposed negatives, and chilling the solution to about 40°F will greatly *retard* the development of overexposed plates. In many cases this is better than addition of chemicals.

Under Exposure.—Some brands of plates can be improved when they are decidedly underexposed, by soaking for fifteen minutes in a weak solution of formalin. After the plate is thoroughly rinsed it should be redeveloped in a weak metol developer at 120°F. Great care must be observed to avoid "fogging" the plate.

Black and White Tones.—These can be obtained by the use of ferrous oxalate as a developer.

A	Neutral oxalate of potassium .	1 oz.
	Potassium bromide	2½ gr.
	Hot water (distilled)	5 oz.
B	Ferrous sulphate	2 dr.
	Hot water (distilled)	2 oz.

For use mix 1 part of "A" solution with 2 parts of "B" and pour evenly over the plate, giving the pan a rocking motion, as long as detail is visible. Then rinse and fix in sodium hyposulphite.

Development After Fixing.—After the plate is fixed and washed, use a solution of potassium permanganate to destroy the last of the "hypo," and rinse. Then place the plate in a solution of potassium bromide 10 grams; copper sulphate 10 grams; water 200 c.c. Place the plate after rinsing in a solution of silver nitrate, 2 grams in 1000 c.c. Repeat the process if at first the image is not of the desired strength.

Stains on Negatives.—If the negative is slightly discolored use a solution of chrome alum 45 gr.; water 10 oz.; add a little citric or hydrochloric acid. If the stain is very yellow a solution of potassium persulphate can be used to advantage. This should be one-half per cent solution and the time of exposure should be five minutes. Repeat if necessary.

Rapid Drying.—Lay a piece of fine cambric over the negative and pass a squeegee over it. This will remove almost all of the water. Negatives can also be rapidly dried on racks before an electric fan, or washed with alcohol.

Clearing Solution for Negatives.—When negatives are developed over a long period of time they sometimes become stained. For "pyro" negatives J. H. Taylor suggests a clearing solution which will do the work in one-half minute. It can be used repeatedly.

Alum	2 oz.
Hydrochloric acid	2 fl. oz.
Boracic acid	1 oz.
Water	32 fl. oz.

Hardening Bath.—Professor Namias carried out exact tests with thirteen standard formulae, and recommends the following hardening bath as the best.

Chrome alum solution 1½%	50 c.c.
Hypo solution . . . 50 %	50 c.c.
Sodium acetate . . . 2.5 grams	

Removal of "Hypo."—The best eliminator of hypo is plenty of cold running water over a period of about an hour. It can be eliminated in about five minutes by means of a

faintly pink solution of potassium permanganate. The permanganate solution is added drop by drop to the wash water until a permanent pink remains, showing that all of the hypo has been destroyed.

The Camera.—A catalogue of any optical company will furnish a description of the camera for general microscopic work.

Satisfactory results, however, can be gotten from "home made" apparatus at only a fraction of the cost, since the objective and eyepiece of the microscope become the lens system of the camera.

Fig. 17. Camera with special eyepiece for focussing. (Will Corp.)

A stationary frame 10 inches higher than the top of the microscope, so made that a standard plate holder will slide in and out, is essential. To this frame a "light tight" extension can be fastened so that it can be fitted snugly over the eyepiece. A ground glass plate can be used for focussing, and you have a camera. Since it usually takes several minutes for an exposure when filters are used the quick shutter is not essential.

When funds are available it is wise to get the best equipment possible. There are some adjustments in the standard camera that are very convenient and are difficult to reproduce in the workshop.

CHAPTER IV

Qualitative Analysis

For convenience of the analyst the elements may be grouped into the following divisions. The classification is based upon what precipitating reagent is used to bring about characteristic crystallization.

Div. 1. (A)

THE HALIDE GROUP.—(Simple chlorides precipitated by dilute HCl.)

Silver, mercury (valence 1), lead, thallium.

(B)

(Double and complex chlorides precipitated with CsCl or RbCl.)

Sn, Sb, Bi, Te, Pt, Au, (If sufficiently concentrated Cu, Co, Fe, Pb, Hg, Ni, Al, Mn, Zn, Cd, Ir, Os, Pa, Ru may also be made to crystallize.)

(C)

(Fluorides precipitated by HCl and NH_4F or some soluble fluoride.)

Ti, Si, Ta, Zr, Al, Li, B , Ba.

Div. 2. (The double thiocyanate group precipitated by $K_2Hg(CNS)_4$.

Zn, Cu, Co, Cd, Fe, Ni, Ag, Pb, Mn, Au, Be.

Div. 3. THE SULPHATE GROUP.—

(A) Double sulphates (alums) precipitated by cesium sulphate.

Aluminum, iron (valence 3), chromium, (indium, gallium, not easily crystallized).

(B) Simple sulphates precipitated by sulphuric acid.

Calcium, strontium, barium, thorium, (bismuth, lead, Hg^1.)

(C) Double sulphates (not alums).
Bismuth, sodium, potassium, cerium and rare earths.

Div. 4. The Oxalate Group.—
Rare earths, Mn, Cd, Zn, Be, Zr, Ca, Sr.

Div. 5. The thallium group.—Precipitated by thallous nitrate in combination with some additional reagent when necessary.
Thorium, molybdenum, tungsten, uranium, platinum, gold.

Div. 6. The Miscellaneous Group. — Magnesium, arsenic, phosphorous.

Div. 7. The Fiber Group. (With ZnS wool fiber.)
In acid soln.
Yellow—Sn, As, Cd.
Orange—Bi, Sb.
Brown—Ag, Bi, Sb, Hg, Pb.
Black—Ag, Bi, Cu, Hg, Pb.
Brown (In alkaline soln.) Ni, Co, Mn, Fe.

THE SIMPLE CHLORIDE GROUP

A small drop of dilute hydrochloric acid is conducted into the test drop on the object glass by means of the sampling rod. The precipitate may be:

AgCl, a white amorphous precipitate soluble in ammonium hydroxide and recrystallizing from such a solution in small tetrahedra and cubes. It can also be recrystallized from concentrated HCl.
The presence of silver can be further verified by employing a new drop and precipitating the silver with $K_2Cr_2O_7$ in a nitric acid solution.
It can be determined also as the cyanide and acetate.

TlCl, a crystalline precipitate occurring as cubes or small crosses. $TlCl_3$ forms pale hexagons. (See page 81.)

$PbCl_2$, a crystalline precipitate occurring as prisms, often with forked ends. (See page 81.)

Additional tests should be applied by forming yellow hexagons with KI, or dark cubes of the triple nitrite.

HgCl, a crystalline precipitate which almost immediately becomes amorphous. The addition of ammonium hydroxide causes the formation of black metallic mercury and $Hg.NH_2.Cl$.

Additional tests should be made with potassium dichromate, which forms a red granular precipitate and occasionally small red crosses.

WO_3 The addition of hydrochloric acid to some compounds of tungsten will cause the separation of yellow tungstic acid on heating.

Silver

	Limits in Micro-milligrams (.001 milligram)
As AgCl	.1
As $Ag_2Cr_2O_7$	.15

The general chemistry of silver and its industrial uses are widely known. For this reason no great discussion is necessary here. The nitrate of silver is quite soluble (227.3 parts in 100 of water at 19.5°C). The chlorate dissolves in about 10 parts of water, the acetate is less soluble, and the sulphate dissolves with even greater difficulty.

Almost all silver salts are soluble in thiosulphate solutions of the alkali metals. Many cyanides such as KCN dissolve silver salts. Silver sulphide is an exception to the general rule.

Silver is usually detected by precipitation as silver chloride. This precipitate is readily soluble in ammonium hydroxide and to some extent in concentrated hydrochloric acid. From the ammoniacal solution three and six sided crystals can be obtained, from the hydrochloric acid solution small cubes predominate. Sulphuric acid slowly trans-

poses silver chloride. Mercuric nitrate gradually converts it over into the nitrate and becomes mercuric chloride. The successful worker should keep these facts in mind.

Silver is precipitated from its solutions by metals higher in the electromotive series. In some instances beautiful branches like those of a growing tree will be formed of the metallic silver. This is typical if metallic magnesium is employed.

Laboratory Exercises

1. Allow a small drop of silver nitrate solution to evaporate on a glass slide at room temperature. As the drop approaches dryness carefully examine the crystalline deposit with the microscope. Become familiar with the crystallization of silver nitrate from dilute and concentrated solutions.

2. Place a small drop of silver nitrate solution on a glass slide and add a trace of hydrochloric acid. Decant the liquid from the silver chloride and dissolve the precipitate in ammonium hydroxide. Allow the solution to concentrate at room temperature. The crystals of silver chloride should be examined by the highest available power of the microscope. Note the three and six sided crystals.

   Try recrystallizing the silver chloride from hot concentrated hydrochloric acid. Small cubes will appear.

3. To a small drop of silver nitrate add a trace of nitric acid. By means of the pointed glass rod draw into this a solution of ammonium or potassium dichromate. Use a medium power of the microscope and watch the growth of $Ag_2Cr_2O_7$ crystals. They become dark red as thickness develops. These are triclinic. Orthorhombic crystals of Ag_2CrO_4 may also appear. (Fig. 18.)

4. Place a small drop of silver nitrate on a glass slide and add a trace of ammonium hydroxide. Then add a very small amount of arsenic acid solution. If the red crystals of silver arsenate do not appear in a few minutes

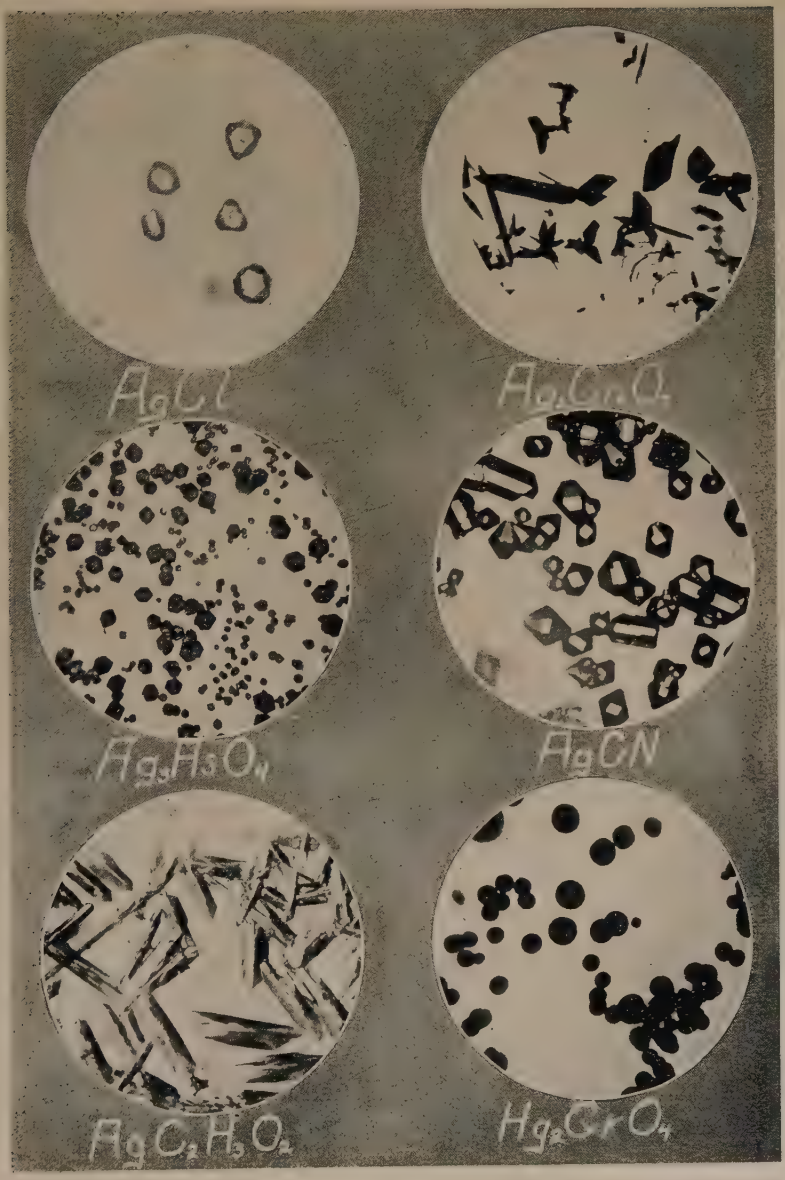

Fig. 18.

add more of the reagent. Avoid a large excess of ammonium hydroxide, unless recrystallization is desired.

5. Place a small drop of concentrated solution of silver nitrate on a glass slide. Add a small amount of acetic acid and allow the preparation to concentrate at room temperature. Examine the drop for clear-cut crystals of silver acetate, having a mother of pearl luster.

6. In a small crucible place a fragment of potassium cyanide and add a trace of dilute sulphuric acid. Lay over the crucible a glass slide with a hanging drop of silver nitrate exposed to the escaping gas. Needles and prisms of silver cyanide will very quickly form. (See page 77.)

7. Precipitate silver chloride in the presence of thallium, lead and mercury of valence one. Dissolve the lead and thallous chloride in hot water and decant. Remove the silver chloride from mercurous chloride with ammonium hydroxide and examine this ammoniacal solution as it concentrates for crystals of silver chloride.

8. Attempt to identify silver as a chromate in the presence of lead or mercury of valence one.

9. In an agate mortar grind together a finely divided mineral of silver with charcoal and sodium carbonate. Heat the mixture on a charcoal stick by means of the blowpipe until a bright bead is formed. Dissolve the small bead in nitric acid and test a drop of the solution for silver as described in 2.

10. Draw the edge of a silver coin across a mineralogy streak plate. (If such a plate is not available the bottom of a porcelain dish will answer the purpose.) Dissolve a portion of the streak with hot nitric acid and quickly transfer a drop of the solution to a glass slide. Test for silver as a chromate. (3).

11. To a drop of a solution containing silver add a fragment of metallic magnesium. Note the growth of silver crystals.

Thallium

	Limits in Micro-milligrams (.001 milligram)
As TlCl	.16
As TlI	.03
As Tl_2PtCl_6	.008

Chemistry.—Thallium is a metal so soft that it will mark paper, and when freshly cut has a bright luster. Its structure is crystalline and exists in two forms, the transition temperature being 226°. Thallium may be kept under water that is oxygen free, but in the air it is slowly oxidized, the rate of oxidation increasing rapidly as the temperature is raised. At red heat it decomposes water. It reacts with sulphur, selenium, tellurium, phosphorous, antimony, arsenic, and the halogens. It is readily soluble in nitric and sulphuric acids, slowly in hydrochloric. In double salts such as $K_2SeO_4.ZnSeO_4.6H_2O$, univalent thallium readily replaces potassium but the resulting compounds are *opaque*. Oxidizing agents, such as bromine and potassium persulphate or permangante oxidize thallous salts to the thallic condition. These in turn can be reduced by stannous chloride and sulphurous acid. Thallic salts tend to hydrolize in water.

Detection.—A green line (λ.5350) appearing in the spectroscope is characteristic of thallium. Univalent thallium is precipitated by soluble chlorides, and the resulting precipitate is soluble in hot water. In this respect it resembles lead. If the concentration of the thallium is very low, small microscopic cubes occur (12μ). At a higher concentration crosses, varying in size (40– 120μ) may appear. These crystals are black by transmitted and white by reflected light. Sulphuric and nitric acids are injurious. When these are present sodium acetate may be added with advantage. Strong nitric acid may cause oxidation of the thallous chloride to the thallic salt.

Alkaline molybdate solutions will precipitate six-sided

plates (50μ). From higher concentrations clusters of needles are produced. This reaction is more fully described under the heading, "Molybdenum."

Chloroplatinic acid gives a very fine crystalline precipitate. The yellow octahedra are about one half the size of the corresponding caesium compound.

Thallous compounds are readily precipitated by potassium iodide. The solubility is very low (1:4500) and the largest aggregates seldom reach a size greater than 15μ.

Thallic chloride is more soluble than the corresponding univalent salt. It may be recrystallized from hot water and will appear as large six-sided plates (25–40μ).

Laboratory Exercises

1. Place on a clean glass slide a drop of very dilute solution of thallous nitrate and allow it to evaporate slowly. Study the shape of the crystals when they appear, and observe their behavior with polarized light.

   (These crystals may often appear when not sufficient reagent is added to the thallous nitrate to cause complete precipitation.)

2. Place on a clean glass slide a small drop of very dilute solution of thallous nitrate. Add to this a trace of dilute hydrochloric acid. If the solution is sufficiently dilute small clear cut cubes appear. Examine the preparation with medium magnification. Try evaporating the solution to dryness by holding the slide over the micro-burner, and recrystallizing from hot water. Note the behavior of the crystals with transmitted and reflected light.

3. Repeat Exercise 2, but use a more concentrated solution of thallous nitrate. Crosses should appear. The bars of the crosses are usually at right angles. Sometimes an effect of "flying birds" is produced. Try recrystallizing the preparation from hot water. (See page 81.)

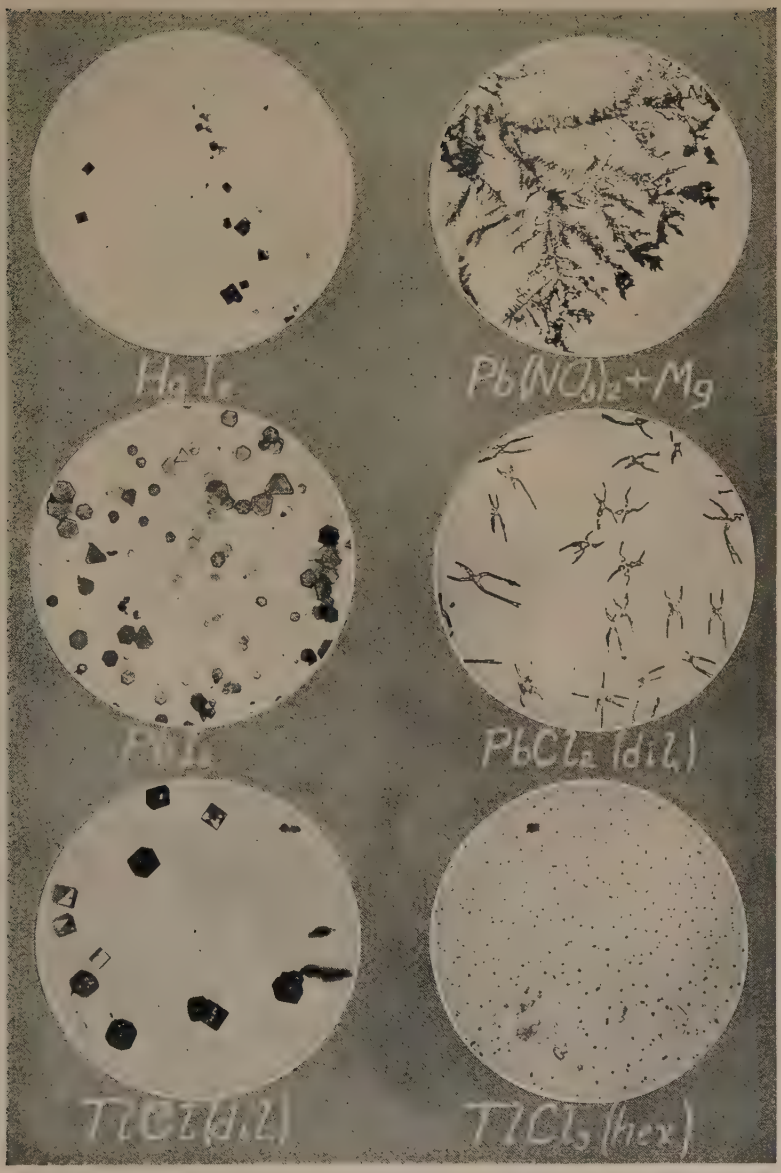

Fig. 19.

4. Oxidize a drop of thallous nitrate to the thallic condition by means of potassium permanganate or potassium persulphate. Extract the residue with water and to this solution add a trace of hydrochloric acid. Allow the preparation to approach dryness. Note the appearance of six-sided plates of *thallic chloride*.
5. To a solution containing a mixture of thallous and silver nitrates add a dilute solution of hydrochloric acid. Warm gently and decant the clear liquid from the silver chloride residue. Allow this decanted liquid to slowly concentrate. Examine the preparation for crystals of thallous chloride.
6. Repeat Exercise 5, using lead nitrate instead of silver nitrate and observe the crystallization of lead chloride and thallous chloride in the presence of each other.
7. Study with the microscope the appearance of the precipitate produced in dilute solutions of thallous nitrate by
   1. Potassium iodide
   2. Potassium dichromate
   3. Platinic chloride
   4. Potassium cobaltic nitrite
8. Note the green color imparted to the flame of the microburner by thallium compounds.

Lead

	Limits in Micromilligrams (.001 milligram)
As $PbCl_2$	.3
As PbI_2	.2
As $PbSO_4$	.04
As $PbCO_3$	.06
As $PbCrO_4$	.1
As $Cs_2CuPb(NO_2)_6$	.03

Solubility.—Most of the compounds of lead are insoluble in water, the nitrate and the acetate being the chief exceptions to the general rule. Fixed alkalies precipitate lead from solutions, the precipitate being soluble in an excess of

the reagent. The halides of lead are soluble in hot water and the sulphate is soluble in ammonium salts of acetic, citric and tartaric acids.

Triple Nitrite Reaction.—This reaction will reveal the presence of .03 μ gr. of lead. The test drop should be slightly acid with acetic acid and then fragments of sodium acetate, copper acetate and potassium nitrite should be added in order. The small squares and cubes that appear have the composition $K_2CuPb(NO_2)_6$, and are black by transmitted light. The presence of rubidium, cesium or thallous compounds increases the delicacy of the reaction. If the presence of lead is doubtful a small fragment of thallous nitrate should be added and the preparation re-examined for the appearance of the characteristic cubes.

The light brown cubes of the nickel salt should not be mistaken for the triple nitrite of lead, and it must be remembered that there is a very insoluble double nitrite of cobalt and potassium which occurs as a brown powder or small cubes and octahedra. (See page 121.)

The presence of mineral acids is injurious, a large excess of lead causes too sudden a precipitation and too many small crystals. Too much potassium nitrite readily dissolves the precipitate.

The Iodide Reaction.—The test drop containing a trace of nitric acid should be lead by the point of a glass rod into a solution of potassium iodide. Bright yellow six sided plates will almost immediately appear and grow to an appreciable size. By recrystallizing these from hot water larger crystals can be obtained. An excess of potassium iodide causes the formation of a double iodide that eventually crystallizes out in large clear six sided plates. Behrens is of the opinion that lead iodide is not hexagonal but orthorhombic.

If the solution of lead iodide is acid, and contains also bismuth and antimony, a red or orange colored powder may form. The lead iodide can be removed by recrystallizing from hot water. (See page 81.)

The Chloride Reaction.—If lead only is present in the test drop it can be detected quite readily by means of a trace of hydrochloric acid. The slender prisms are orthorhombic and polarize strongly. If the solution is dilute the crystals appear with forked ends, often resembling pincers. (See page 81.)

Lead chloride is more soluble in nitric acid than in water and should therefore be recrystallized. The chlorides of ammonia and potassium are injurious, forming bundles of very thin needles.

Lead chloride also forms a number of double chlorides. The double chloride of lead and cesium can be mistaken for cesium chlorstannate.

The Chromate Reaction.—A solution of potassium chromate added to a hot test drop of a lead solution that has been acidified with nitric acid will form short, slender yellow needles and rhombs. From neutral solutions a yellow powder is formed which may be converted into a basic chromate by the addition of a small amount of caustic alkali. This basic chromate is crystalline. This is also an excellent means for tracing chromium.

The Oxalate Reaction.—Lead oxalate will precipitate from hot solutions in the form of rectangular rods, and from cold solutions in the form of grains and small crosses. There are so many insoluble oxalates which form crystalline deposits that this method is not very satisfactory for the identification of lead.

The Bicarbonate Reaction.—Lead can be precipitated as the carbonate by adding a solution of sodium bicarbonate to the test drop. Very characteristic branched rods are formed. If ammonium carbonate is used as a reagent the crystallization will take place after a few minutes standing.

The Sulphate Reaction.—Tiny rhombic crystals of lead sulphate are formed by adding a dilute solution of sulphuric acid to the test drop containing lead. It forms more

readily when the sulphide of lead is digested in concentrated nitric acid. The sulphate of lead can be separated from strontium and barium by digesting in caustic alkali, and the lead can be precipitated by sodium bicarbonate.

The Nitrate Reaction.—Alloys and other compounds rich in lead can be made to produce clear, highly refractive octahedra of lead nitrate by digesting the material in concentrated nitric acid, in which the lead nitrate is much less soluble than in water.

Exercises With Lead

1. Dissolve a crystal of lead nitrate in a drop of water and allow the solution to evaporate slowly. Study the shape and general appearance of the crystals of lead nitrate.

2. Determine the approximate refractive index of these crystals by immersion method. Note their behavior between crossed nicols.

3. To a dilute solution of lead nitrate add a trace of hydrochloric acid. Examine the preparation for forked crystals of lead chloride. The crystals should give parallel extinction (Orthorhombic system) and are more abundant when recrystallized from hot water. When recrystallized from hot hydrochloric acid thin rhombic plates may appear. Prismatic forms are common.

4. Place a drop of solution containing both potassium chloride and lead nitrate on the glass slide and add a trace of dilute hydrochloric acid. Note the bundles of thin crystals formed, and their irregularity. Repeat, using ammonium chloride, and also prepare the double chloride of cesium and lead.

5. Try the effect of adding the chloride of antimony, bismuth or tin to a drop of lead nitrate solution. Note the increased complexity of the double chlorides formed with lead.

6. Acidify a dilute solution of lead nitrate with nitric acid and add to a drop of this a very small drop of potassium dichromate solution. Examine the preparation for stout prisms and clusters of slender needles.
7. Precipitate crystals of lead iodide from a solution of lead nitrate to which has been added a trace of nitric acid. Avoid an excess of potassium iodide. Recrystallize these six sided plates from hot water and note their increased size.
8. Note the effect of the presence of iodides of bismuth and antimony on the lead iodide in acid solutions (reddish powder).
9. To a neutral solution of lead nitrate add a small fragment of a copper salt, some sodium acetate and an excess of potassium nitrite. Note the dark brown cubes of the triple nitrite. The addition of either cesium or thallous compounds increases the delicacy of the test.
10. Recrystallize a small amount of lead sulphate from hot nitric acid and note the very small plates and rhombs of lead sulphate.
11. Precipitate lead oxalate from a hot solution. Notice the rods and small crosses formed.
12. To a drop of very dilute solution of lead nitrate add a drop of sodium bicarbonate solution. Examine the preparation for small branched rods.

Mercury

	Limits in Micromilligrams (.001 milligram)
As Hg_2Cl_2	.25
As Hg_2CrO_4	.5
As HgI_2	.075
As double thiocyanate	.04

The Thiocyanate Reaction.—A solution of mercuric salts to which has been added a fragment of cobaltous acetate will give a deep blue precipitate with ammonium thio-

cyanate. If a trace of zinc also is present the crystallization is more rapid but lighter in color. If copper is substituted for cobalt the crystallization will be in the form of yellow needles.

The Codeine Sulphate Reaction.—A solution of codeine sulphate which has been acidified with hydrochloric acid will precipitate a solution of mercuric chloride in the form of rhombic crystals or clusters of needles. A high concentration of the mercuric chloride favors the formation of the rhombic form.

The Iodide Reaction. — Potassium iodide will bring about almost immediate crystallization of red, tetragonal crystals of mercuric iodide. The reagent should not be added in excess due to the formation of the readily soluble double iodide, $HgI_2 . 2KI$. Mercuric iodide is soluble in hot water and can be recrystallized in the form of ruby plates and pyramids. (See page 81.)

Laboratory Exercises With Mercury

1. Precipitate HgCl by concentrated hydrochloric acid and observe the crystallization. Notice how the slender needles rapidly become granular.
2. Add ammonium hydroxide to a precipitate of HgCl. The black deposit is mercury.
3. To a drop of hot mercurous nitrate solution, acidified with nitric acid add a drop of potassium dichromate solution. Notice the round granular precipitate and small red crosses.
4. Repeat Ex. 3, having a small amount of silver nitrate present with the mercurous nitrate.
5. Add acetic acid or a solution of sodium acetate to a drop of mercurous nitrate and study carefully the crystallization of mercurous acetate.
6. In a small glass sublimation tube place a mercury compound intimately mixed with dry sodium carbonate. (The

tube should be closed at one end.) Apply heat. Examine the distillate with the microscope for free mercury.

7. To a solution of mercuric chloride add a very tiny fragment of potassium iodide. Examine the red border around the fragment of potassium iodide for tetragonal crystals of HgI_2. Avoid excess of KI.
8. To a solution of codeine sulphate acidified slightly with hydrochloric acid add a solution or a small fragment of $HgCl_2$. Notice the starlike clusters of slender prisms and also the rhombs when $HgCl_2$ is added in excess.
9. To a solution of mercuric salt add a fragment of cobalt acetate and then a solution of KCNS. Notice the deep blue crystals of cobalt mercuric thiocyanate.

DOUBLE CHLORIDE GROUPS AND TEST LIMITS

(Precipitated by CsCl or some suitable chloride)

		Limits in Micro-milligrams (.001 milligram)
Antimony	CsCl	.08
	$H_2C_2O_4$	1.00
	Barium tartrate	1.00
	As sodium pyroantimonate	.5
Bismuth	With KHC_2O_4	.3
	RbCl	.13
	$KHSO_4$	.3
	KI & H_2O	.4
Iridium	As Rb_2IrCl_6	.3
Nitrogen	Traced in nitrites with KI	.25
	As $(NH_4)_2PtCl_6$	.1
	As $NH_4MgPO_4.6H_2O$	.05 NH_3
	Cyanogen as Prussian blue	.07
Osmium	With cesium chloride	.1
	As $K_2OsO_4.2H_2O$	.1
	As $N_4H_{12}OsCl_2$	.05

PLATINUM	As $N_2H_4(NH_4)_2.Cu.PtCl_4$	.06
	As K_2PtCl_6	.6
	As Rb_2PtCl_6	.2
	As Tl_2PtCl_6	.004
RUTHENIUM	With CsCl	.8
	Traced with NH_4CNS	1.2
SELENIUM*	Precipitation with Mg	.1
	With KI	1.0
TELLURIUM	With Mg	6.00
	With CsCl	.3
	With KI	.6
TIN	With $AuCl_3$	.07
	With oxalic acid	1.
	With CsCl	.45
RHODIUM	As $K_3Rh(NO_2)_6$	.09
CESIUM	$SnCl_4$	1.6
	As silicomolybdate	.25

OTHER DOUBLE CHLORIDES

Besides the double chlorides mentioned above, a number of other double chlorides are possible. If to a concentrated solution of copper chloride solid cesium chloride is added, short and long bi-pyramidal prisms will be formed. These may be either red with excess copper or yellow from more dilute solutions. They may show two pyramids only or prism faces, with or without pyramids. (See page 101.)

A concentrated solution of ferrous chloride will produce with cesium chloride beautiful yellow prisms not unlike the copper. Ferric chloride will give yellow rhombs or prisms that are bi-pyramidal. Often the yellow rhombs appear six-sided due to the incomplete development on two ends.

A concentrated solution of cobalt chloride will give large blue rhombs and hexagons with solid cesium chloride.

*Selenium is placed here only for convenience. It properly belongs in the miscellaneous group.

There are other double chlorides of cesium with di- and tri-valent elements, but they form with difficulty and only when the drop approaches dryness.

Platinum

The Element.—Platinum is usually found on the market as a grayish-white metal, very difficult to fuse except in the oxyhydrogen blowpipe or by means of the electric current. It exists in two other allotropic conditions: *platinum black* which is formed by the reduction of platinum salts in acid solutions, and *spongy* platinum which is obtained by igniting ammonium chloroplatinate. These two forms are used for the surface condensation of gases.

Platinum is readily soluble in aqua regia, from which solution yellow crystals of chloroplatinic acid ($H_2PtCl_6.6H_2O$) can be obtained by evaporation. The metal is not soluble in pure single acids, but is oxidized by such oxidizing agents as permanganate, chlorates and dichromates.

Compounds.—The action of aqua regia on platinum oxidizes the platinum to a valency of four. It can be reduced to the lower valency of two by potassium iodide, stannous chloride, or potassium oxalate. It is reduced to the metal from solution by such reducing agents as formic acid, or metallic zinc in acid solution. The most common compounds of platinum at the higher state of oxidation are those of the chloroplatinates, corresponding to the general formula (R_2PtCl_6). At the lower state of oxidation platinum forms a number of compounds such as $K_2Pt(CN)_4.4H_2O$. Many salts formed by the action of ammonia on platinum compounds are known and are used to detect small quantities of platinum.

Detection of Platinum.—Potassium chloride will precipitate almost immediately bright yellow octahedra from concentrated solutions of chloroplatinic acid. If platinum is present even in traces the crystals will eventually appear. In extreme cases it may be necessary for the preparation to be evaporated to dryness.

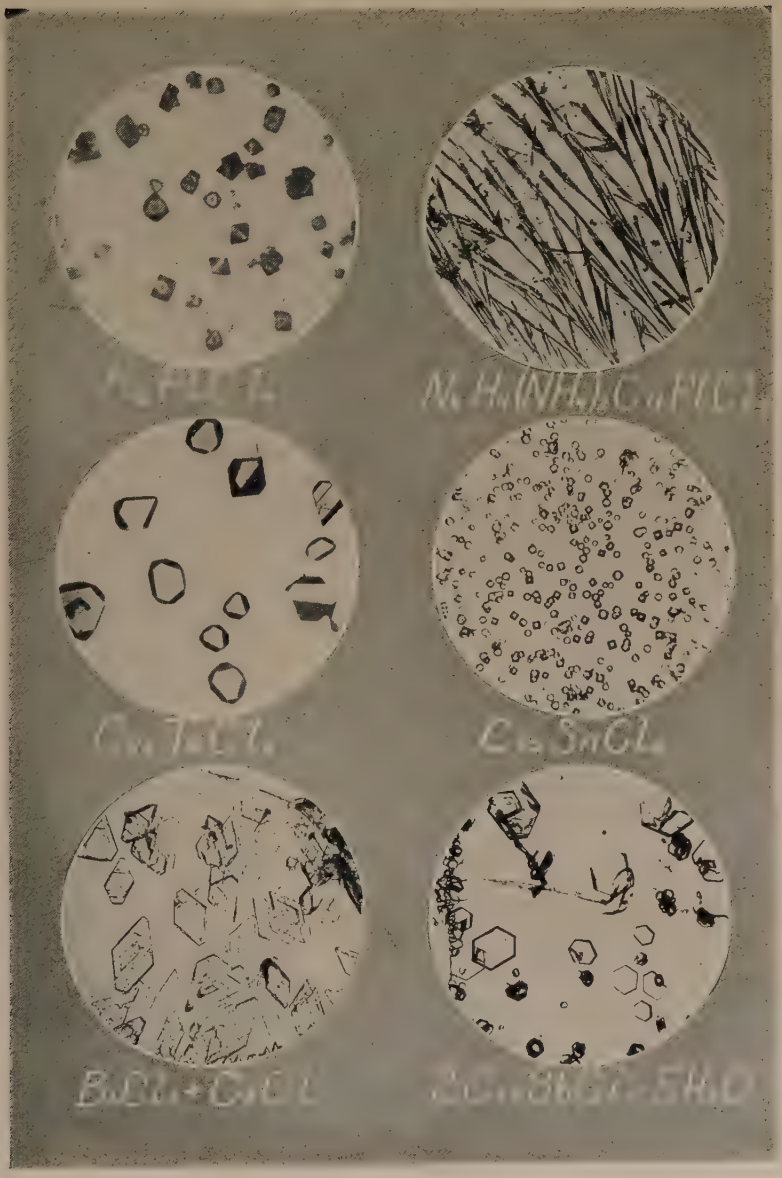

Fig. 20.

Rubidium chloride will form similar crystals but smaller than the corresponding potassium compound. This reagent makes it possible to detect .03 per cent of platinum. Cesium chloride gives a still more delicate reaction but a high power must be used to recognize the individual crystals.

Thallous nitrate will show the presence of platinum in a dilution of 1 : 18,000. The crystals appear as a yellow powder if the solution is fairly concentrated. Iridium tetrachloride is reduced by thallous nitrate to a dirty green compound.

Chloroplatinates should not be confused with chloropalladate and chloroiridate. The presence of iridium tetrachloride produces a reddish color in the crystals of chloroplatinate.

Platinous Chloride.—If the platinum is present in the lower state of oxidation it can be detected as the chloroplatinite of cupridiammonium. If the solution contains chloroplatinic acid it can be reduced with stannous chloride. A fragment of a copper salt is added to the platinous solution, an excess of ammonium chloride and last a large amount of ammonium hydroxide. From concentrated solutions long violet needles will immediately appear. If the solution contains less than .01 per cent of potassium chloroplatinate short needles will appear which in a few minutes will develop sufficient thickness to show the distinct violet color. Palladous compounds do not give a similar reaction.

Green needles of chloroplatinite of platinodiammonium can be produced by adding ammonium hydroxide to a solution of potassium chloroplatinite.

The Platinum Metals.—The ores containing platinum may also contain osmium, ruthenium, iridium, rhodium and palladium. The ore is digested for several hours with aqua regia and filtered. The residue may contain a natural alloy called iridosmine (osmiridium). This is given separate treatment, as described under B.

A (SOLUTION)

The solution should be concentrated to a syrupy condition and digested several times with hydrochloric acid. As evaporation proceeds more acid should be added. Add sufficient water to dissolve the solid matter and then add a saturated solution of ammonium chloride. After a few minutes filter off the crystalline precipitate, wash with ammonium chloride solution, in which the platinum compound is not soluble, dry the crystals and ignite. This will be spongy platinum. Dissolve a small amount of this in aqua regia, and add a drop of potassium chloride solution. If this last reaction is carried out on a glass slide and the preparation examined under the microscope the characteristic yellow octahedra of potassium chloroplatinate will be seen.

The addition of metallic zinc to the solution from which the ammonium chloroplatinate was precipitated will reduce iridium, palladium and rhodium to the metallic state. Filter off the precipitated metals and wash them with boiling water and add aqua regia. Filter the preparation. Rhodium and iridium will be in the residue, palladium and any gold will be in the filtrate. The filtrate should be evaporated and the mass dissolved in hydrochloric acid. The addition of mercuric cyanide will precipitate the palladium. The palladium compound should be filtered off and ignited. Any gold present would be in the filtrate and can be reduced to metallic state by addition of $FeSO_4$.

The ignited palladium can be converted to the tetrachloride and tested with a small amount of potassium iodide. This gives a dark brown precipitate soluble in excess of the reagent. If ammonium hydroxide is added to palladium iodide small orange colored needles will appear and in a short while yellow dendrites.

Light brown dendrites of chloride of palladiammonium ($N_2H_6PdCl_2$) can be made by the addition of ammonium chloride and excess of ammonium hydroxide to a solution of palladium salts.

Ammonium thiocyanate alone will not give indication of the presence of palladium. If thallous nitrate is also added

a brown precipitate will form which will recrystallize from hot water as large rectangular dendrites and scales. If the solution is very dilute rectangular crosses and prisms are formed.

Iridium and Rhodium.—The iridium and rhodium residues left after the palladium is dissolved in aqua regia should be boiled with 10% KOH and well washed. To the mixture should be added a like amount of sodium chloride and the whole heated in an atmosphere of chlorine at a temperature of 440°C. The mass should be dissolved in water and the excess sodium chloride crystallized out. The liquid should then be heated with nitric acid and a saturated solution of ammonium chloride added. This will precipitate the iridium. If the quantity involved is very little rubidium chloride will give almost instantaneous precipitates. The crystals are very small bright red octahedra. Rhodium will be in the filtrate. This should be evaporated and ignited to metallic rhodium.

Rhodium salts are precipitated by potassium nitrite from both acid and alkaline solutions. Cesium chloride gives a more delicate test if added to the reaction. Six sided plates, some of which appear halved and bright yellow in color, are characteristics. Six poked stars may also be present.

B

(The residue after digesting the crushed ore with aqua regia and filtering.)

The residue should be fused with zinc as long as zinc fumes are expelled. The mass is then ground and heated with barium peroxide. It is then cooled, treated with aqua regia and one-fourth of the volume is distilled. The distillate contains osmium as osmic acid. The undistilled liquor contains ruthenium, rhodium, and a little platinum.

Osmium.—The distillate containing osmium should be redistilled into ammonium water. Hydrogen sulphide from this solution will precipitate OsS_4. This can be converted into metallic osmium by heating in a closed crucible. The

amorphous metal may be readily dissolved in fuming nitric acid. The crystalline form is insoluble in acids, and must be fused with a mixture of sodium peroxide and nitrate before a solution can be made. The finely divided metal reacts with oxygen readily forming OsO_4 which has a very disagreeable odor and produces temporary blindness.

Microscopic Test.—Solutions of osmic acid in hydrochloric acid give a white crystalline precipitate with cesium chloride. Osmic acid also gives violet octahedra when reduced by alcohol, in the presence of potassium hydroxide which dissolves the osmic acid forming a light brown solution. These octahedra are very clear cut and are very characteristic.

If ammonium chloride is added to the alkaline solution of the osmite it is transformed into yellow dendrites. After these have crystallized the addition of potassium ferrocyanide will give an intense purple tint.

Ruthenium.—The undistilled liquor, after the removal of the osmium, is treated with sulphuric acid and filtered. This removes the barium sulphate. Evaporate to dryness and remove the silica. To the solution add a little aqua regia and a strong amount of ammonium chloride. This precipitates ammonium chloriridate and also some platinum salts, which are filtered off. Metallic zinc is added to the filtrate which precipitates rhodium and ruthenium as a fine powder. This is fused with KOH and potassium nitrate and the melt extracted with water. Rhodium is found in the insoluble portion and can be filtered off. The ruthenium is found in the filtrate as potassium ruthenate. The addition of nitric acid precipitates ruthenium as ruthenium oxide. Metallic ruthenium is obtained on ignition.

Solutions of ruthenium in aqua regia give very small reddish brown grains with cesium chloride. Thallous nitrate gives yellow grains of about the same size.

Concentrated solutions of ruthenium give a purple color with soluble thiocyanates. Iron, cobalt, platinum and palladium interfere.

When ruthenium trichloride is treated with hydrogen sulphide a blue color is obtained.

A violet precipitate (K_2RuCl_5) is precipitated from concentrated solutions by potassium chloride.

Laboratory Exercises

If solutions of platinum, ruthenium, iridium and osmium are available

Prepare

(1) K_2RuCl_5; K_2PtCl_6; $K_2OsO_4.2H_2O$; ammonium chloriridate; potassium-rhodium nitrite; cesium rhodium nitrite in ammoniacal solution.

(2) From solutions of platinous chloride prepare the chloroplatinite of cupridiammonium ($N_2H_4(NH_4)_2Cu.PtCl_4$) described under Platinum.

Tellurium

Crystalline tellurium has a silvery white appearance. The amorphous tellurium precipitated by reducing agents from solutions is a black powder. It burns on charcoal with a green flame forming a white sublimate of tellurium dioxide. It is not acted upon by hydrochloric acid. It is acted upon by hot sulphuric acid, giving under these conditions a violet red color. It is readily oxidized to H_2TeO_3 by either aqua regia or nitric acid. It is reduced to the metallic state by such reducing agents as sulphurous acid, stannous chloride or hydrazine. The reduction is brought about in an acid solution, but an excess must be avoided. It can be separated from selenium by acidifying the solution with strong hydrochloric acid and then adding the reducing agent. On warming the preparation the selenium is precipitated and the tellurium remains in solution.

Chemistry of Tellurium.—The chemistry of tellurium is very much like that of sulphur and selenium. As indicated by its position in the periodic table it is more metallic than either of these. It forms tellurides with the metals, and tellurites and tellurates are both known. It forms chlorides

and bromides by direct union with the halogen. With fluorine it reacts directly, or TeF_4 may be formed by HF on TeO_2.

Selenium

Extraction.—The commercial sources of selenium are flue dusts and anode muds. The selenium can be obtained (1) by dissolving the soluble material with water and then dissolving the residue in aqua regia. (2) By fusing the material with sodium carbonate and dissolving the selenide and selenite in water. (3) By digesting the solution with KCNS. From either of the three solutions the selenium can be precipitated in the absence of oxidizing agents by the addition of sodium sulphite in a strong hydrochloric acid solution.

The Metal.—When precipitated in the above manner the element at first appears red. On further digestion it goes over into the gray modification. The element is soluble in carbon disulphide. From a warm solution it will crystallize out in red plates (monoclinic). From a cold solution the plates will be orange-red and different in form.

Steel gray hexagonal crystals of selenium can be obtained by heating the element to a temperature of about 145°C and allowing it to cool slowly. This is the metallic form, insoluble in carbon disulphide.

The compounds of selenium resemble those of sulphur. The true and pseudo alums are isomorphous with the corresponding compounds of sulphur.

Selenium is a poor conductor of electricity. Heating increases the conductivity. Exposure to light for a fraction of a second greatly increases this property.

Laboratory Exercises

Tellurium

1. Dissolve a small amount of tellurium in nitric acid and evaporate to dryness. Dissolve the TeO_2 in a small amount of hydrochloric acid.

2. To a drop of this solution add a fragment of cesium chloride and note the yellow-green crystals of cesium chlorotellurite (Cs_2TeCl_6). Repeat, using rubidium chloride or potassium chloride. Notice that these crystals are larger and less refractive than those of K_2PtCl_6. The tellurium compound is decomposed by water. (See page 91.)
3. To some of the crystals prepared as described in (2) add a drop of potassium iodide solution. The chlorotellurite is blackened. Potassium chlorostannate would have been stained yellow by potassium iodide.
4. To some of the elementary tellurium add a drop of strong sulphuric acid solution and warm. A reddish violet color indicates tellurium.
5. Dissolve a small amount of tellurium dioxide in potassium hydroxide. Potassium tellurite is formed (K_2TeO_3). Now add sulphuric acid until the first precipitate formed dissolves. Then add potassium permanganate. Telluric acid has been formed (H_2TeO_4).
6. Try the effect of heating a slightly acid solution of tellurium with such reducing agents as sulphurous acid or stannous chloride.

Selenium

1. Dissolve some metallic selenium in concentrated nitric acid. Evaporate to dryness, and add water. H_2SeO_3 is formed. To this solution add potassium permanganate. The selenious acid is oxidized to selenic acid (H_2SeO_4).
2. To a drop of this solution add a barium chloride solution. Barium selenate is formed.
3. To a drop of the selenious or selenic acid add sodium sulphite and strong hydrochloric. Notice the formation of red selenium. This may later become the gray modification.
4. To a solution containing a mixture of selenious acid and tellurous acid add strong hydrochloric acid and then sodium sulphite. The selenium is precipitated as a red

powder. The tellurium is in solution. Test for its presence with cesium chloride.

5. Add a drop of strong sulphuric acid to a small amount of selenium and note the green color on warming.
6. Selenium as an impurity in sulphuric acid can be detected by adding a drop of the mixture to codeine phosphate. A green color is evidence of the presence of selenium.[1]

Antimony

The Element.—Metallic antimony dissolves in nitric acid. If the nitric acid is in too great an excess insoluble oxides will be formed which are soluble in hydrochloric acid. Finely divided antimony will react with excess of chlorine with the production of light, resulting in the formation of $SbCl_5$. The dry and ignited Sb_2O_3 is but little soluble in nitric acid while the freshly precipitated oxide is readily soluble in the hot or cold solution of dilute or concentrated acids. The antiminous oxide is soluble in an excess of fixed alkali, forming metantimonites. Antiminous oxide is formed when antimony compounds are ignited on charcoal by means of the blowpipe.

Detection.—In the wet way antimony is precipitated from solutions that are slightly acid by means of hydrogen sulphide, the orange Sb_2S_3 being formed. This would be soluble in ammonium polysulphide along with the sulphides of gold, platinum metals, tin, arsenic, molybdenum, tellurium and selenium. Digestion with hydrochloric acid, Sp. gr. 1.2 will dissolve the antimony and tin. If a piece of platinum foil and a fragment of metallic zinc are placed in the solution containing the tin and antimony and allowed to touch, the tin will be deposited on the zinc and antimony deposited on the platinum. The antimony deposit can be dissolved in nitric acid, and the solution tested for antimony by the addition of water, forming the SbOCl, or with hydrogen sulphide forming the orange precipitate.

[1] E. Schmidt, Arch. Pharm. 252: 161; C. A. 8: 2990 (1914).

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Microscopic Tests.—All the salts of antimony are decomposed by water with the exception of compounds of antimony with certain organic acids such as tartaric and citric.

A solution of antimony compound will color "zinc sulphide wool" an orange, provided no other element is present which gives a colored sulphide.

Rubidium chloride added to a solution of antimony acidified with hydrochloric acid gives large six sided plates, which in some instances will develop toward hexagonal pyramids as a limit. Cesium chloride will form a more insoluble double chloride and therefore is a more delicate reagent. The addition of potassium iodide will produce a yellow color in the double chloride.

Very characteristic crystals of sodium pyroantimonate can be prepared from antimony compounds by igniting the sample with five times its volume of potassium nitrate at red heat until at least half of the nitrate has been volatilized. Wash the mixture with cold water and boil with a dilute solution of potassium hydroxide. Sodium chloride is then added and the preparation examined for the crystals which grow to considerable length from dilute solutions. A drop of alcohol speeds up the crystallization. Niobium should be absent.

Barium chloride will precipitate clusters of large six sided plates from strong solutions of tartar emetic. The crystals have the composition $(Ba(SbO)_2C_4H_4O_{12}.2H_2O$. The great solubility necessitates concentrating weak solutions almost to dryness. This can be used as a test for barium in the absence of other members of the alkali earth group.

Laboratory Exercises—Antimony

1. To a solution of antimony compound add water. A white precipitate indicates the presence of such elements as bismuth or antimony, which easily hydrolize. Note the effect of organic acids such as tartaric acid on hydrolysis of antimony compounds.

$CuCl_2 + C_9Cl$
$FeCl_3 + C_9Cl$
$AuCl_3 + TlNO_3$
$AuCl_3 + C_9Cl$
$K_2C_2O_4 \cdot 2H_2O$
$Ba(SbO)_2C_8H_4O_{12}$

Fig. 21.

2. Place in a drop of antimony solution a thread of "zinc sulphide wool." Note the orange color (Sb_2S_3) appearing in the thread.
3. Place a compound of antimony in the distilling crucible. Add a fragment of zinc and some sulphuric acid. Cover the crucible with a glass slide carrying on the under surface a hanging drop of silver nitrate. Notice the blackening of the silver nitrate due to the formation of Ag_3Sb. If arsenic is thought to be present the hydrogen should be generated with aluminum and sodium hydroxide.
4. Prepare a slide of sodium pyroantimonate crystals as described on page 100. Notice that they polarize parallel to the edges of the prism. From dilute solutions large crystals develop.
5. Precipitate clear six sided plates from a drop of antimony solution with cesium chloride. Repeat, using rubidium chloride, and notice the increased size of the crystals of the double chloride. Small orange crystals will appear after the separation of the double chloride, if a small amount of potassium iodide is added to the test drop. (See page 91.)
6. Small fragments of barium chloride added to a solution of potassium antimony tartrate will cause the formation of clusters of thin hexagons and rhombs. This can be used as a test for barium if the other alkali earths are absent. (See page 101.)
7. Oxalic acid will precipitate antiminous oxalate from antimony solutions. Tin, lead, bismuth and elements giving interfering crystalline oxalates should be absent.

Bismuth

The Compounds.—The hydroxide is soluble in acids but not in alkalies. Nearly all of the bismuth compounds hydrolyze in water with the formation of oxy-salts in the absence of organic acids. Hydrogen sulphide precipitates bismuth from solution and the resulting bismuth sulphide is soluble in dilute nitric acid. If this solution is made alkaline with

ammonium hydroxide bismuth hydroxide is precipitated, and any copper or cadmium present would remain in solution. Sodium or potassium stannate reduce all bismuth salts to metallic bismuth, and all salts of bismuth are oxidized to the pentavalent condition by H_2O_2 or by chlorine in alkaline solution. Metallic bismuth will precipitate platinum, silver, mercury and gold from solution. It will be precipitated from solution by the elements above it in the electromotive series.

Microscopy of Bismuth.—Bismuth is soluble in nitric acid and aqua regia. It is insoluble in hydrochloric. From concentrated solutions acidified with hydrochloric acid rubidium chloride will precipitate almost immediately stout prisms. From more dilute solutions six sided plates and rhombs develop. The crystals obtained with cesium chloride are less soluble and give a more delicate test for traces of bismuth.

(b) If the bismuth compound is converted to the sulphate and a small amount of potassium sulphate added together with a trace of nitric acid to prevent hydrolysis, clear six-sided plates and coffin shaped crystals almost immediately appear. Ammonia gives similar crystals. (See page 141.)

(c) When sodium sulphate is substituted for potassium in (b) short needles appear almost instantly if the solutions are concentrated. These will develop considerable length in a short time. Bismuth sulphate is an excellent reagent to use in the detection of potassium and sodium in the presence of each other. (See page 141.)

(d) Bismuth oxalate can be precipitated from solutions by means of oxalic acid. A double oxalate of potassium and bismuth can be obtained by the addition of potassium oxalate and recrystallizing the precipitate from hot solutions. The crystals are very small and it is difficult to distinguish them from the oxalates of calcium and strontium.

Laboratory Exercises—Bismuth

1. Dissolve a fragment of stannous chloride in an excess of of caustic alkali. To this solution add a drop of a solu-

tion containing bismuth. A black deposit of metallic bismuth will be formed.

2. To a drop of a solution containing bismuth add a small fragment of metallic copper. A blackening of the copper indicates the presence of an element lower than copper in the electromotive series.
3. To a drop of bismuth solution acidified with hydrochloric acid add water. A white precipitate of the oxychloride indicates the presence of bismuth, antimony or tin.
4. To a drop of a bismuth solution acidified with hydrochloric acid add a concentrated solution of rubidium chloride. Six sided plates and large thin rhombs will form very quickly. From very concentrated solutions stout prisms will form almost immediately. These will gradually be changed into rhombs on standing. (See page 91.)
5. To the preparation described in (4) add a small amount of potassium iodide. Small red hexagons develop.
6. Convert the bismuth compound to the sulphate. Add a drop of nitric acid to prevent hydrolysis, and then add a strong solution of potassium sulphate. Six sided plates develop very quickly. Some will be shaped like coffins.
7. Repeat (6), using sodium sulphate instead of potassium.

Tin

The Metal.—Hot, concentrated hydrochloric acid dissolves tin rapidly, forming stannous chloride and hydrogen. It can also be dissolved by hot concentrated sulphuric acid or aqua regia. Nitric acid attacks it rapidly, forming metastannic acid ($H_{10}Sn_5O_{15}$). Tin is also attacked by the fixed alkalies and by both chlorine and bromine.

Compounds of Tin.—An excess of water decomposes stannous chloride with the formation of $SnO.SnCl_2$. Liquid stannic chloride reacts with water, forming the hydrate $SnCl_4.3H_2O$. Stannic salts are decomposed by water. Stannic sulphate and stannous nitrate are deliquescent. Stannous sulphide is brown, stannic sulphide is yellow. Both

are insoluble in water but soluble in hydrochloric acid or in fixed alkalies. They are not soluble, however, in ammonium hydroxide which distinguishes them from arsenic.

White stannous hydroxide ($Sn(OH)_2$) is precipitated by alkali hydroxides and carbonates. This is soluble in excess of fixed alkali hydroxides, insoluble in alkali-carbonates and ammonium hydroxide (Distinction from antimony).

Stannic acid (H_2SnO_3) is precipitated from stannic solutions by alkali hydroxides. This is soluble in excess of alkali hydroxides but insoluble in ammonium hydroxide and the alkali carbonates.

Sodium thiosulphate does not form a precipitate with chlorides of tin. (Separation of tin from arsenic and antimony, Lessen, Z., 1888: 27-218.)

Neither oxalic acid nor ammonium oxalate precipitate stannic chloride. (Hausmann & Lowenthal, A., 1854: 89, 104.) Stannous chloride forms a white precipitate with oxalic acid if the solution is nearly neutral. This will dissolve in large excess of ammonium oxalate.

Reduction of Tin.—Compounds of tin mixed with sodium carbonate or potassium cyanide can be reduced to globules of tin by heating on charcoal by means of the blowpipe.

Solutions of tin are reduced to the metallic state by cadmium, aluminum, zinc or magnesium. Stannic salts are reduced to stannous by metallic tin, copper or iron. (Allen, J. C., 1872: 25, 274.) Metallic tin reduces silver, mercury, bismuth, copper, platinum and gold to the metallic state. Auric chloride is reduced to the metallic condition by stannous chloride forming the "Purple of Cassius." (Max. Muller, J., Dr., 1884: 30, 252.)

Detection of Tin.—By means of the gold, zinc wire couple .00003 grams of tin in solution can be detected. (Rideal, C. N., 1885: 51, 292.)

Stannous salts added to solutions of mercury compounds cause the formation of either black metallic mercury or white mercurous compounds. An alkaline solution of stannous chloride gives also a black precipitate with solutions

of bismuth compounds. Stannous chloride also produces a black precipitate in ammoniacal solutions of silver nitrate. This method can be used even if lead, antimony, aluminum, chronium or zinc are present.

Microscopy of Tin.—Potassium iodide added to a concentrated solution of stannous chloride gives a yellow precipitate, changing with an excess of the reagent to rosettes of dark orange needles. Concentrated solutions of potassium iodide will precipitate yellow stannic iodide, soluble in water, forming a colorless solution. Free iodine is not liberated from HI by stannic salts. (Distinction from arsenic and antimony; Harroun, J. C., 1882: 42, 661.)

Stannous chloride added to a solution of ammonium molybdate gives a blue colored solution of the lower oxides of molybdenum.

Cesium chloride gives almost immediately a crystalline precipitate (Cs_2SnCl_6) with stannic chloride, consisting of small cubes and octahedra. Rubidium chloride gives larger crystals but is not so sensitive. If copper and iron are present red or yellow double chlorides of these elements with cesium may appear. Lead forms a colorless double chloride resembling the tin. A large number of the elements such as Sb, Pt, Al, Os, Ir, Pd, Te, Zn, Fe, Bi form double chlorides with cesium, and these must not be confused with the Cs_2SnCl_6 crystals. (See page 91.)

Yellow cubes and octahedra, more insoluble than the colorless cubes and octahedra of the cesium chlorostannate can be formed by adding a trace of potassium iodide to the stannic solution after the cesium chloride has been added. They are probably Cs_2SnI_6 or a solid solution of iodostannate in the chlorostannate.

THE FLUORIDE GROUP AND TEST LIMITS

		Limits in Micro-milligrams (.001 milligram)
ALUMINUM	CsCl (See Sulphates)	.35
	NH_4F	.3
BORON	As KBF_4	.2
FLUORINE	As Na_2SiF_6	2.00
	As $BaSiF_6$	.7
LITHIUM	As Li_2CO_3	.36
	As LiF	.25
SILICON	With Na_2SiF_6	.05
	As silicomolybdate	.004
TITANIUM	With $K_2TiF_6.H_2O$	6.0
	As $Rb_2TiF_6.H_2O$	1.0
TANTALUM	As K_2TaF_7	6.0
	With NaOH	1.2
ZIRCONIUM	With KHC_2O_4	.06
	As Rb_3ZrF_7	.5
BARIUM	As $BaSiF_6$ (See Sulphates)	.09

SILICON

SILICIC ANHYDRIDE.—Silicon dioxide (SiO_2) occurs in almost all of the geological formations. In many instances it is in the form of the silicate, in combination with various bases. The compounds of silicon are so numerous that no attempt is made to tabulate them here.

CHEMICAL REACTIONS.—Silicon dioxide is insoluble in water and acids but is soluble in the fixed alkalies, forming silicates. From such solutions the addition of an excess of mineral acid precipitates silicic acid (H_2SiO_3), a white gelatinous solid. Some silicates are decomposed into SiO_2 by boiling in concentrated hydrochloric acid, some form silica gel and some are insoluble. Solutions of alkali silicates precipitate all other metallic salts from solution.

DETECTION.—The finely ground material containing silicon is treated with HF or a mixture of ammonium fluoride and HCl, upon a varnished slide. PRECAUTIONS SHOULD

BE OBSERVED TO AVOID INJURING THE LENS OF THE MICROSCOPE. Sodium fluosilicate crystallizes in six sided plates and rosettes, resembling flowers with six petals. The crystals have a rose tint. This tint occurs, however, with the sodium fluozirconate, titanate, borate, etc., but all of these require a longer time for crystallization. Potassium fluosilicate crystallizes in colorless cubes.

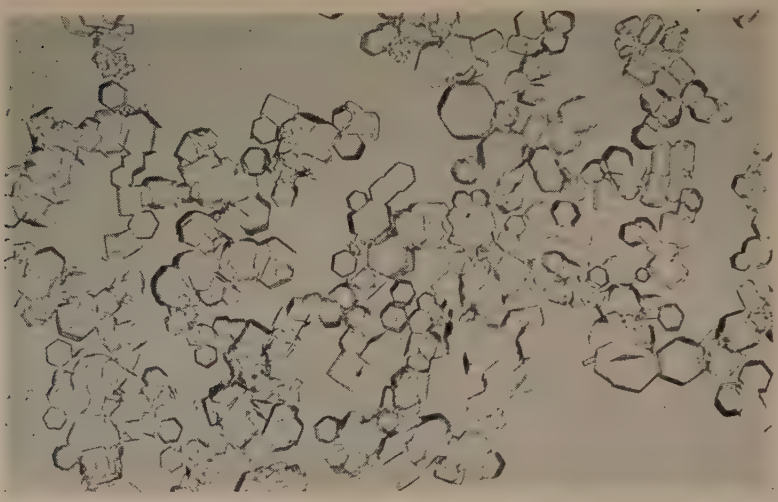


Fig. 22. Sodium fluosilicate (Faint Pink).

Silicomolybdate of rubidium can be obtained by fusing the sample of silicon with five times its volume of sodium carbonate and dissolving the fused mass in water. To this solution add ammonium molybdate and nitric acid. Silica from the glass slide must be avoided, and yellow grains of ammonium phosphomolybdate must not be taken for the silicon compound. The test is sensitive to the presence of .004μ gr. of Si.

Lithium

The Element.—Lithium is found in combination with other elements in many minerals. It is widely but sparingly distributed in minerals, also in springs and the ashes of plants.

Lithium is the lightest of the metals. It is usually prepared by electrolysis of the chloride. It reacts with water, forming LiOH and evolving hydrogen.

In some respects lithium resembles the elements of Group II in the periodic table (alkali earth group). The solubility of its carbonate, fluoride, hydroxide and phosphate is considerably less than those formed by the other members of the alkali family. In this respect it more closely resembles the calcium compounds. The chloroplatinate and picrate are readily soluble in water. In this respect also it is different from potassium salts.

Detection.—Traces of lithium can be detected by means of the spectroscope. Its bold red line is readily recognized.

A white precipitate is obtained when soluble phosphates are added to solutions of lithium salts. The preparation should be heated. The precipitate is more soluble in ammonium chloride than in pure water. (Distinction from magnesium.) The crystals may appear as grains, rhombs and rectangles.

Lithium fluoride crystals vary in form depending upon what soluble fluoride is used for precipitation of the lithium. With sodium, potassium or ammonium fluoride cubic crystals are usually obtained. Excess of ammonium chloride produces rectangular rosettes. (Behrens.)

The best crystalline test for lithium is with ammonium carbonate. Clusters of needles are produced from dilute solutions. The crystallization begins around the margin of the drop, and as it approaches dryness the star-like clusters form more or less uniformly.

The addition of a drop of water to the crystals distinguishes them from ammonium sulphate. The latter compound is readily soluble in water.

Zirconium

The Element.—Zircon, a silicate of zirconium, is the chief mineral of zirconium. The element is never found native, but can be prepared in the laboratory by fusing po-

tassium zirconium fluoride with potassium. It has also been prepared by electrolysis of the chloride.

Chemical Reactions.—Zirconium oxide (ZrO_2) may be prepared by fusing zircon with a fixed alkali. Zirconium chloride is prepared by passing chlorine over ZrO_2 mixed with charcoal. The chloride is soluble in water from which solution it can be precipitated by alkali hydroxides and sulphides as $ZrO(OH)_2$. Metallic zirconium is very slowly soluble in acids other than hydrofluoric. In this, however, it is readily soluble.

Detection.—A saturated solution of potassium sulphate will precipitate potassium zirconium sulphate. If this is precipitated while hot the precipitate is insoluble in water or hydrochloric acid. (Distinction from Th or Ce.)

Zirconium salts are precipitated on warming with $Na_2S_2O_3$. (Separation from Y, Nd & Pr.)

Potassium acid oxalate will precipitate a double oxalate ($K_4Zr(C_2O_4).4H_2O$, in the form of small rhombs resembling strontium oxalate. The test will detect .01% of zirconium sulphate. Hydrochloric acid will dissolve the crystals and is therefore injurious. If titanium dioxide is also present it will not give a crystalline precipitate except on the addition of sodium acetate. The titanium precipitate is in the form of small rods.[1]

Solutions of zirconium sulphate or chloride will give with ammonium fluoride and a grain of rubidium chloride crystals very similar to those of cesium alum. Sometimes a trace of HCl is necessary. From concentrated solutions rectangular prisms may also be formed. Behrens suggests K_3ZrF_7 as the composition of these crystals. A varnished slide should be used for the test.

Boron

The Element.—Boron does not occur native. In the laboratory it can be prepared in either the amorphous or crystalline state. It has been prepared by electrolysis and also by fusing the oxide with sodium, magnesium or alumi-

num. The amorphous variety is brown, is a nonconductor of electricity, is odorless and tasteless.

Solubility.—The alkali borates are soluble in water. The borates of the other metals are but slightly soluble. In most instances they form metaborates of which $AgBO_2$ is an example.

Acids such as hydrochloric (mineral acids and many organic acids) convert borates into boric acid. This acid dissolved in alcohol burns with a green flame.

Detection.—Borates slightly acidified with HCl turn tumeric paper red. The red becomes green on the addition of a drop of alkali.

Borates fused in the inner flame of the blowpipe with $KHSO_4$ give a green color to the outer flame. A brighter green is obtained from solid borates after they are intensely heated if the powder is moistened with sulphuric acid and glycerine and burned on a platinum wire.

Ammonium fluoride and hydrochloric acid will precipitate boron from solutions if potassium chloride is present. The pale hexagons, rhombs and octagons of the potassium fluoborate (KBF_4) are converted into prismatic crystals by recrystallization from water. (Behrens.)

Titanium

Properties.—It does not occur free in nature, but can be prepared by heating the chloride with metallic sodium. When heated in air it burns brilliantly, and will combine directly with the nitrogen. Hydrogen is evolved when the metal is dissolved in acids. Titanium tetrachloride is a colorless liquid which reacts with water, forming titanic acid and hydrochloric. The presence of the latter helps to keep the former in solution. TiO_2 is the principal oxide.

Chemical Reactions.—Compounds of titanium are soluble in hydrofluoric acid. When such a preparation is concentrated with HF alone the titanium tetrafluoride is volatilized. The presence of sulphuric acid prevents volatilization of the TiF_4, but under these conditions any silicon pres-

ent will vaporize as SiF_4. (Separation from silicon.) Alkali sulphides, hydroxides and carbonates precipitate titanium from solutions as an hydroxide.

Detection.—Titanium compounds fused in the blowpipe with microcosmic salt give in the reducing flame a yellow bead. On cooling it becomes reddish and if ferrous sulphate is added to the fusion the bead becomes blood red.

Hydrogen peroxide added to solutions of titanium will give an orange color.

A double fluoride of potassium and titanium ($K_2TiF_6.H_2O$) can be prepared by fusing TiO_2 with KF. The double salt is but little soluble in water but is readily soluble in HCl. Behrens suggests fusing the insoluble titanium compound with sodium carbonate and ammonium fluoride. The product is treated with dilute HCl on a varnished slide and a grain of a potassium compound added. Rectangles, octagons and six sided plates are formed. The reaction is more sensitive if cesium or rubidium is substituted for potassium.

Laboratory Exercises With Fluorides

1. Sodium Silicofluoride.—Prepare crystals of sodium silicofluoride (pink hexagonal plates and prisms) by dissolving a fragment of silicon compound in hydrofluoric acid or a mixture of ammonium fluoride and hydrochloric acid. A grain of sodium chloride must be added. If six petalled rosettes appear the silicon is present in large quantities.

2. Rubidium Silicomolybdate. — Fuse some SiO_2 with sodium carbonate and dissolve the preparation in water. To this add ammonium molybdate and nitric acid. If yellow grains of the phosphorous or arsenic compound appear these can be removed by heating. Precipitate the silicon by adding a fragment of rubidium chloride.

(Potassium chloride will precipitate complex molybdates of bismuth, columbium and tantalum but not silicomolybdates. The complex molybdates of zirconium, tin and titanium have a different appearance.)

Fig. 23.

3. Potassium Fluotantalate.—To a solution containing tantalum, add ammonium fluoride, hydrochloric acid and finally a grain of potassium chloride. Slender prisms will slowly appear around the margin of the drop.

(Fusion with sodium fluoride aids in getting tantalum compounds into solution.)

4. Potassium Fluozirconate.—Fuse a tiny amount of a zirconium compound with potassium fluoride. Dissolve the mass in hot water and allow the preparation to concentrate by evaporation. Examine the test drop for small rectangular prisms. (K_2ZrF_6.)

To a test drop containing a soluble zirconium compound add ammonium fluoride, hydrochloric acid and a fragment of rubidium chloride. From concentrated solutions rectangular prisms are obtained, from more dilute solutions octahedrons and six sided crystals are formed. (K_3ZrF_7.) (See page 113.)

5. To a test drop containing a soluble zirconium compound add a fragment of potassium acid oxalate. (Avoid free acid.) Small tetragonal crystals will be formed. (See page 146.)

(If sodium acetate is absent titanium compounds will not crystallize under these conditions.)

6. Rubidium Fluotitanate. — Decompose an insoluble titanium compound by fusion with sodium fluoride. To the assay add hydrochloric acid and a fragment of potassium chloride. Rhombs, hexagons and octagons will slowly form.

7. Ammonium Fluoaluminate.—To a very dilute solution of an aluminum compound add a fragment of ammonium fluoride. Small rods and octahedra will develop slowly around the circumference of the drop. ($AlF_3.3NH_4F$.)

(Lithium and also sodium will produce only a granular precipitate. Behrens.)

8. Potassium Fluoborate.—To a test drop containing a boron compound add a grain of ammonium fluoride, a drop of hydrochloric acid and finally a fragment of po-

tassium chloride. Rhombs, hexagons and octahedra predominate. (KBF_4.) (See page 113.)

(Small amounts of silica can be removed by adding barium acetate.)

9. LITHIUM FLUORIDE.—Study the crystallization of lithium fluoride when produced by KF, NaF, NH_4F, respectively. The first produces cubes, the second may give also hexagonal prisms, the third cubes or rectangular rosettes, if used in excess. (See page 113.)

LITHIUM CARBONATE. — When lithium is present in small amounts ammonium carbonate will form small bundles of needles. (Li_2CO_3.) The reagent should be added in the solid form and some time allowed for crystallization. (See page 113.)

(Platinic chloride, bismuth sulphate nor phosphomolybdic acid give crystalline precipitates with lithium salts.)

10. BARIUM SILICOFLUORIDE.—To a slightly acetic acid solution of barium add a small amount of ammonium silicofluoride. Well developed rods appear almost immediately. Heating aids the reaction.

(Calcium and strontium do not give a similar reaction.)

GROUP IV

THE DOUBLE THIOCYANATE GROUP AND TEST LIMITS

(Precipitated by ammonium mercuric thiocyanate from a slightly acid solution)

Ag, Co, Cu, Fe″, Zn, Cd, Pb, Au, Be

	Precipitated with	Limits in Micromilligrams (.001 milligram)
CADMIUM	$NaHCO_3$	.01
	$H_2C_2O_4$	—
	As double thiocyanate	1.
	$K_6Fe_2(CN)_{12}$	.03
COPPER	As triple nitrite	.03
	With $K_4Fe(CN)_6$	.1
	As double thiocyanate	.1
	As cuprous iodide	.05

		Limits in Micro-milligrams (.001 milligram)
Cobalt	As double nitrite	.1
	As double thiocyanate	.3
	As double phosphate	.02
	As $Co_2Cl_6.10NH_3$	.2
Iron	With $K_4Fe(CN)_6$	.07
	With NH_4F	.2
	With barium oxalate	.1
	As $Fe(CNS)_2.Hg(CNS)_2$	—
Zinc	With $NaHCO_3$	.01
	With oxalic acid	.1
	As double thiocyanate	.1
	With $K_6Fe_2(CN)_{12}$	.05

Precautions.—Too great a concentration of the element under observation produces masses of crystals which are not easily recognized. This is particularly true in making the test for zinc and copper. The test is made by leading a drop of the reagent into a neutral or a slightly acidified solution of the substance investigated. Either potassium or ammonium mercuric thiocyanate may be used as a precipitating reagent. The presence of alkali substances is injurious to this compound reagent, and heating is harmful. Too great a concentration of reagent must also be avoided, and free nitric acid should not be present.

The Preparation of Ammonium Mercuric Thiocyanate[1]

To a saturated solution of mercuric nitrate containing a trace of nitric acid add a 5% solution of the thiocyanate solution. Either ammonium, potassium or sodium thiocyanate may be used. The potassium salt makes the most stable compound. This 5% solution should be added as long as precipitation continues. This precipitate should be

[1]Recommended by Dr. E. M. Chamot.

washed until no test is gotten for either mercury with KI or the thiocyanate with $FeCl_3$. This mercuric thiocyanate should be added to the 5% solution of the ammonium thiocyanate until the mercuric thiocyanate fails to dissolve. Do not heat. When saturation is reached add a little of the ammonium thiocyanate and then evaporate on the water bath until crystallization is well under way. The crystals should be recrystallized from water. Avoid "burning" during evaporation.

Zinc

The Metal.—Zinc is precipitated from solutions by metallic magnesium, and in turn precipitates Cd, Sn, Cu, Bi, Hg, Ag, Pt, Au, As, Sb, Te, In, Fe, Co, Ni, Pd, Rh, Ir and Os from solutions of their salts. The zinc-copper couple reduces iodates to iodides, chlorates to chlorides, ferric to ferrous salts, nitrites to ammonia, and will lower the valence of manganese to two in the presence of some acid that is non-reducing.

By heating compounds of zinc on charcoal with sodium carbonate before the blowpipe metallic zinc is first formed which is soon converted by the oxygen of the air into zinc oxide, yellow while hot and white when cold. Moistened with cobalt nitrate and reignited this becomes green.

Chemical Reactions.—From solution zinc is precipitated by fixed alkalies as zinc hydroxide, soluble in an excess of the reagent provided the alkali solution is stronger than one tenth normal. Ammonium hydroxide precipitates the zinc hydroxide which is soluble in excess of ammonia or ammonium salts, forming complex zinc ammonia ions.

Alkali carbonates precipitate a basic zinc carbonate soluble in excess of the reagent or fixed alkalies. Alkali cyanides precipitate zinc cyanide which is also soluble in excess of the precipitating reagent. Alkali phosphates precipitate a zinc phosphate soluble in alkali hydroxides and also many acids. The ferro and ferricyanides of the alkali metals precipitate white ferro and yellow ferricyanide of zinc.

Alkali arsenites and arsenates precipitate the corresponding zinc salts which are soluble in fixed alkalies and in acids. Potassium chromate gives a yellow precipitate with zinc solutions, the dichromate does not. Alkali sulphides precipitate zinc from solution as a white sulphide, soluble in dilute acids.

Microchemical Reactions.—If no interfering element is present the most satisfactory method for the detection of zinc is with potassium or ammonium mercuric thiocyanate. The double thiocyanate of zinc and mercury is a rectangular rod belonging to the orthorhombic system. This crystallization can be brought about when the concentration of the reacting substances is sufficiently great. Feather-like crosses are usually formed and can be considered characteristic. The presence of CADMIUM destroys these to a very large extent. Arrowhead crystals often occur under these conditions, and if the amount of cadmium is large zinc cannot be detected by this reagent.

A trace of copper causes the feathery crosses to turn a chocolate brown. More copper renders the crystals black and a large amount of copper results in the formation of black spherical masses. These accompanied by some of the typical yellow crystals of the double salt of copper and mercuric thiocyanate and the white crosses of the pure zinc compound are almost always found in testing mixtures of the two elements.

The presence of cobalt destroys the feathery structure of the crosses when present in appreciable amounts. Traces of cobalt color the crosses a light blue, larger amounts of cobalt interfere.

If ferrous iron is present in large amounts, radiating clusters of yellow prisms somewhat resembling the copper salt will form. The presence of ferric salts causes the zinc compound to assume a reddish brown color. (See page 128.)

Nickel does not interfere with the test for zinc except when present in very large amounts. If manganese is present in sufficient quantity it will have an influence similar to

that of cadmium. COLLOIDS AND ORGANIC ACIDS ALWAYS HAVE AN INJURIOUS EFFECT on this reaction.

PRECIPITATION WITH SODIUM CARBONATE. — Zinc can easily be detected, even in the presence of cadmium, by means of sodium carbonate in slightly acid solution. The cadmium compound is precipitated in the form of minute grains. The first deposit of zinc compound changes in a few minutes to heaps of highly refractive tetrahedra ($8ZnCO_3.3Na_2CO_3.8H_2O$). (See page 128.)

If cadmium is present in large quantities it is best to precipitate from ammoniacal solutions of zinc. The cadmium compound is precipitated at once, the zinc about a minute later. A drop of the clear liquid can be decanted away from the cadmium deposit and allowed to crystallize into the characteristic octahedra of the double carbonate of sodium and zinc. Under these conditions cadmium, calcium cobalt and nickel do not interfere.

PRECIPITATION AS AN OXALATE.—Oxalic acid gives with zinc solutions crystals resembling strontium oxalate even in the presence of some hydrochloric acid. Potassium oxalate gives pyramidal crystals. When the zinc oxalate is dissolved in ammonia and recrystallized large rosettes (500μ) occur. Magnesium, when present forms a double oxalate (hexagonal plates). Cadmium does not interfere except from ammoniacal solutions.

COBALT

CHEMICAL REACTIONS.—Cobalt is precipitated from solutions by soluble arsenites, arsenates, oxalates, cyanides, ferrocyanides, ferricyanides, carbonates and phosphates. The ferro and ferricyanide of cobalt are not appreciably soluble in acid. The cyanide is soluble in excess of the reagent forming a double cyanide. The other precipitates mentioned are soluble in mineral acids and ammonium hydroxide. The presence of ammonium salts aids the latter reaction. Fixed alkali hydroxides precipitate a blue basic

hydroxide, which turns green on exposure to air, and on boiling becomes red. Ammonium hydroxide gives incomplete precipitation. Ammonium sulphide precipitates cobalt sulphide from solutions free of mineral acid. After precipitation it is but little soluble in dilute acids.

Microchemical Reactions.—If the solution is not too dilute blue prisms are obtained almost immediately when a drop of potassium mercuric thiocyanate is led into the test drop containing cobalt. The presence of traces of mineral acids and salts causes elongation of the crystals. Very dilute solutions can be concentrated, or the preparation allowed to approach dryness. The crystals have a tendency to cluster. (See page 121.)

Nickel does not interfere with the test except when present in very large amounts. The influence of zinc has already been discussed. Cadmium causes the formation of larger crystals with a fainter color. (See Cadmium.)

The Double Nitrite.—The double nitrite of cobalt and potassium ($3KNO_2.Co(NO_2)_3.1\frac{1}{2}H_2O$) is formed by adding a solid fragment of potassium nitrite to a neutral or slightly acetic acid solution of cobalt. This test is very delicate, the deposit consisting of exceedingly fine grains. Failure to obtain this test is a sure indication that cobalt is absent. The deposit is black by transmitted light, yellow by reflected.

Color Reactions.—From concentrated solutions ammonium thiocyanate gives a blue color disappearing on dilution. This blue solution may be extracted by a mixture of 25 vol. ether and 1 of amyl alcohol.

A brick red precipitate is obtained by the addition of nitroso-beta-napthol in presence of hydrochloric acid. The precipitating reagent is prepared by digestion in 50% acetic acid.

Potassium xanthate forms a green precipitate in neutral or slightly acid solutions of cobalt salts.

Compounds containing cobalt will color the borax bead an intense blue on ignition.

Fig. 24.

Cadmium

Chemical Reactions.—If such organic substances as citric and tartaric acids are absent fixed alkalies will precipitate from solution cadmium hydroxide, insoluble in excess of the reagent. In this manner it can be separated from zinc and tin. If ammonium hydroxide is used as a precipitating agent the cadmium hydroxide will dissolve in an excess, and on concentration such salts as $CdSO_4.xNH_3$ will crystallize.

Soluble sulphides will precipitate yellow cadmium sulphide from solutions not too strongly acid.

Potassium cyanide precipitates a white cadmium cyanide, soluble in excess of the reagent. Soluble oxalates, phosphates, carbonates and ferricyanides precipitate cadmium from solution, the cadmium compounds thus formed being soluble in mineral acids.

Cadmium colors the borax bead yellow while hot, white when cold. By fusing some potassium sulphide with the bead permanent yellow may be obtained. (Distinction from zinc.)

Microchemical Reactions. — Monoclinic rectangles ($CdC_2O_4.3H_2O$) are formed when a solution of oxalic acid is added to a test drop containing cadmium. The crystals are about 60μ in size and may have truncated ends. According to Haushofer, .34μ gr. of cadmium can be detected in this manner if zinc is absent. The reaction cannot be depended upon in the presence of over 10% of zinc. Under these conditions the cadmium should be precipitated with sodium bicarbonate in ammoniacal solution, the zinc decanted and the remaining cadmium deposit tested with a grain of oxalic acid. (See page 121.)

If ammonia is present the cadmium oxalate will crystallize in the form of large rods and plates.

Potassium mercuric thiocyanate will precipitate colorless prisms pointed at one end. They are several times longer than wide. By zinc they may be masked. (See Zinc.) A trace of cobalt will color the $Cd(CNS)_2Hg(CNS)_2$ a blue,

the intensity depending upon the amount of cobalt present.

Zinc sulphide wool will be stained a lemon yellow if placed in a slightly acid solution of cadmium salts. Arsenic should be absent.

Copper

Chemical Reactions.—Fixed alkalies if saturated will precipitate a deep blue cupric hydroxide. If the alkali is not saturated basic salts will be formed instead. Heating changes the hydroxide to CuO. Ammonium hydroxide added in excess will dissolve the light blue basic salt first formed and gives a deep blue solution from which $CuSO_4.4NH_3$ has been isolated, although the blue solution is thought to contain the copper compound in a hydrated condition. This in itself is a good test for copper. In the presence of alkaline tartrates and certain sugars (glucose) cuprous oxide can be precipitated from copper solutions. Cuprous iodide is formed by the addition of potassium iodide to solutions of cupric salts. Stannous chloride also reduces cupric salts to the cuprous condition. Copper salts are precipitated from solutions by H_2S.

Solubilities.—Ammonium hydroxide dissolves all of the salts of copper except the sulphides. Cuprous salts are insoluble in water, soluble in hydrochloric acid and reprecipitated on dilution. The oxalate, phosphate, ferro and ferricyanides, sulphide, borate, arsenate, tartrate and basic carbonate are insoluble in water; the chloride and chlorate are deliquescent and the acetate efflorescent. The sulphate is comparatively stable. The chloride and nitrate are soluble in alcohol, the sulphate and acetate insoluble.

Color Tests.—Potassium xanthate gives a yellow color with very dilute solutions of copper salts. (One part of copper in 900,000 can be detected.)

Ammonium benzoate (10% solution) completely precipitates copper salts from slightly acid solutions. (Gicci, B., 1884: 17, 2659.)

Solutions containing as little as one hundred thousandth

of copper salts are colored brown by hydrogen sulphide in a slightly acid solution. Under these conditions iron, manganese, cobalt and nickel do not precipitate. If the solution is made alkaline arsenic, antimony and tin do not interfere. Copper sulphide is soluble with difficulty in hydrochloric acid, antimony sulphide is not. The solubility of copper sulphide in potassium cyanide distinguishes it from mercury, cadmium, bismuth, and lead. In nitric acid mercuric sulphide is not readily soluble. Copper sulphide is.

Hydrobromic acid added to cupric solutions and concentrated by evaporation gives a rose-red color. This color test is sensitive to .001 mg. of copper. (Endmann & Prochazka, C. N., 1880: 42, 8.)

Iron wire will become coated with copper even in solutions so dilute as one part in 120,000.

The deep blue color which is formed by ammonium hydroxide with cupric solutions is always a good indication of copper.

Microscopic Reactions. — Potassium mercuric thiocyanate will precipitate from cupric solutions clusters of yellow needles $CuHg(CNS)_4$. The single crystals are often found with a knob in the middle. *Traces* of copper can be detected by the addition of a small amount of zinc salts. Under these conditions the feathery crosses of the zinc compound $Zn(CNS)_2.Hg(CNS)_2$ will be colored a brown by the presence of minute traces of copper.

Copper can be detected as the triple nitrite by reversing the test for lead. (See page 121.)

Potassium ferrocyanide precipitates minute traces of copper.

Iron

The Metal.— Iron is the hardest of the ductible metals. Cobalt and nickel exceed it in tenacity. Finely divided iron burns readily when ignited in the oxygen of the air. In meteorites the element is sometimes found native. For a discussion of the metallurgy of iron the reader must be referred to special texts. Cold concentrated nitric acid forms

passive iron. The metal is soluble in hydrochloric, hot sulphuric and dilute nitric acids.

Solubility.—Ferrous salts in solution gradually change over into ferric compounds, usually basic. These hydrolize in water, giving an acid reaction. Ferrous chloride, iodide, bromide and citrate are deliquescent. The sulphate containing seven molecules of water is efflorescent. The hydroxide, tartrate, tannate, oxalate, borate, phosphate, carbonate, cyanide, ferri and ferrocyanide are insoluble in water.

Ferric chloride is soluble in ether, which permits its separation from aluminum. Ferric sulphate is soluble in alcohol, which permits the separation of ferrous from ferric sulphate. The tannate, borate, sulphite, phosphate, basic acetate and ferrocyanide are insoluble in water. The sulphate, nitrate, chloride and bromide are deliquescent.

Reactions.—Alkali hydroxides precipitate both the ferrous and ferric hydroxides. The former is usually a dirty green due to the presence of ferroso-ferric hydroxide. The ferric hydroxide is a reddish brown. A basic ferric acetate is precipitated by adding soluble acetates to ferric solutions and boiling. Potassium ferrocyanide precipitates "Prussian Blue" from solutions of ferric salts. This is one of the best tests for iron. Potassium thiocyanate forms a blood red solution with traces of ferric salts. Either of these reactions can be used for the detection of iron with the microscope.

Potassium mercuric thiocyanate gives clusters of yellow prisms with ferrous solutions if the solution is not too dilute. These have not such slender points as the yellow copper compound, and more closely resemble the colorless cadmium double salt obtained with the same reagent. If ferric iron is present the prisms will be a reddish brown, and as crystallization proceeds many will have curled ends. (See p. 128.)

Yellow crystals of cesium ferric alum can be prepared by adding to the test drop a fragment of cesium sulphate and allowing the preparation to concentrate. The yellow octa-

hedra may appear colorless if not allowed to develop thickness. The growth is very slow.

The crystallization of barium oxalate is strongly modified by the presence of ferric chloride. The small prisms of the oxalate are converted into tufts of brown curling hairs. Platinic chloride produces a like modification.

Glucinum

From concentrated solutions of glucinum crystals resembling those of ferrous iron and cadmium have been obtained. They are colorless and much larger than those of the other double thiocyanates. As a test for small amounts of glucinum it would be valueless. Glucinum will be described fully in the oxalate group.

Lead

Lead under certain conditions and concentrations will form long rods with potassium mercuric thiocyanate. The presence of such should lead the investigator to make confirmatory tests as chloride, nitrite, etc.

Gold

According to Behrens gold can be made to replace mercury in the formation of the double thiocyanates. A small amount of ammonium thiocyanate produces a reddish powdery precipitate, a larger amount produces rosettes of a pink color which dissolve in ammonia and also in hot ammonium thiocyanate. This colorless solution precipitates either zinc or cobalt in a form similar to the analogous compounds of mercury. The zinc-gold double thiocyanate is bright yellow, the cobalt a dark blue-green.

Silver

Silver gives only an amorphous precipitate with $K_2Hg(CNS)_4$. It masks the crystallization of the other members if present. It should be removed with HCl.

Nickel

As the preparation becomes dry, nickel may appear as tiny grains with $K_2Hg(CNS)_4$.

Laboratory Exercises

1. Observe the crystallization produced when a very dilute solution of zinc is led into a drop of a *strong* solution of potassium mercuric thiocyanate. (*Rods* of the zinc compound should be formed.)
2. Make characteristic crosses of the zinc mercuric thiocyanate by using same reagents, but dilute.
3. Note the effect of adding a trace of mineral acid. Note also the injurious effect of the presence of organic radicals.
4. Repeat experiment 2, adding a trace of copper salts, and notice the brown stain on the zinc crosses, or the "rounded effects" if the copper is added in larger quantities.
5. Repeat experiment 2, using a trace of cobalt as impurity and then reverse the experiment, using an excess of cobalt and a trace of zinc.
6. Repeat 5, using cadmium instead of cobalt.
7. Repeat 5, using ferrous iron instead of cobalt.
8. Repeat 5, using ferric iron instead of cobalt.
9. Repeat 2, using potassium mercuric thiocyanate respectively with mineral salts of

Ferrous iron	Lead (concentrated soln.)
Ferric iron	Nickel (concentrated soln.)
Cadmium	Glucinum (concentrated soln.)
Copper	

10. To a solution of gold chloride add an excess of ammonium thiocyanate and warm. The resulting solution

Fig. 25.

should be colorless. To this solution add a trace of zinc. Yellow crystals resembling those obtained in 2 will be formed. If cobalt is substituted for zinc dark greenish blue crystals will be formed. Gold has replaced mercury in these double thiocyanates, the form of the crystals remaining that of the analagous mercuric salts.

11. To a mixture of cadmium and zinc add sodium bicarbonate in an ammoniacal solution. Decant the zinc mother liquor and test the residue for cadmium with oxalic acid. Allow the mother liquor to crystallize and examine for typical crystals of the double carbonate of sodium and zinc.

12. (a) Prepare the triple nitrite of Cu. (b) The double nitrite of cobalt. (c) The triple nitrite of nickel. (d) The oxalate of Cd. (e) The influence of ferric salts on crystallization of barium oxalate.

THE SULPHATE GROUP AND TEST LIMITS

Div. A. Ca, Ba, Sr, Bi, Ag, Pb, Hg, Th.
Div. B. Al, Cr, Fe‴, In, Ga.
Div. C. Na, K, NH_4, Cs, Rb.
Div. D. Rare earths.

DIVISION A

		Limits in Micro-milligrams (.001 milligram)
Barium	H_2SO_4	.05
	As $BaSiF_6$	.09
	As $BaCrO_4$	.08
	As double tartrate of Ba and Sb	.45
Calcium	As sulphate	.04
	As tartrate	.03
	$K_4Fe(CN)_6$	.015
	$H_2C_2O_4$	.06
Potassium	As K_2PtCl_6	.05
	As Phosphomolybdate	.3
	As $K_2Bi(SO_4)_3$	.2

		Limits in Micro-milligrams (.001 milligram)
Sodium	With uranyl acetate	.8
	As Na_2SiF_6	.16
	As $Na_3Bi(SO_4)_3$	.04
Strontium	With H_2SO_4	.2
	As $SrCrO_4$	.8
	As tartrate	.4
	As $SrCO_3$	.4
Sulphur	As $CaSO_4.2H_2O$	.2
	As cesium alum	.12
	As $PbSO_4$	.006

General Procedure.— The addition of dilute sulphuric acid to a solution containing the elements of Div. 1 will precipitate lead, barium, and strontium at once. Silver, mercury and bismuth sulphates will crystallize on concentrating the drop. Under certain conditions described in detail under thorium (page 155) that element may be made to form a characteristic precipitate. As the drop begins to concentrate the needles of calcium sulphate dihydrate quickly appear.

If no precipitate is obtained with dilute sulphuric acid, and no characteristic crystallization is developed after concentrating the preparation, tests for the presence of Div. B may be undertaken. The addition of a solid fragment of cesium sulphate to a solution containing members of Div. B results in the formation of typical alum crystals. The formation of the chrome and iron alums is rather slow. Aluminum forms colorless octahedra, chromium (val. 3) violet, and iron yellow. The colors are developed as the crystals develop thickness. Rubidium sulphate may be used instead of cesium but the test is not so delicate. If the chloride is used a trace of sulphuric acid should also be added.

Bismuth sulphate is used to detect the presence of Div. C. Since cesium had been added as a reagent in detecting Div. B, it necessarily follows that a *new* test drop should be taken.

If certain of the rare earths should also be present the addition of soluble sulphates in the presence of Div. C will

result in the formation of double sulphates of the rare earths.

Calcium

The Chemical Reactions.—The element will react with water forming an hydroxide with the evolution of hydrogen. Ignition of the hydroxide, carbonate, nitrate and all organic compounds of calcium result in the formation of the oxide.

Fixed alkali hydroxides will precipitate calcium from solution as calcium hydroxide. Ammonium hydroxide gives no precipitate with calcium solutions, a soluble complex salt being formed. Soluble carbonates will precipitate calcium carbonate, which will be soluble in water saturated with carbon dioxide. On digestion with an alkali carbonate calcium sulphate will be converted to the carbonate. (Distinction from barium.)

Alkali sulphides precipitate calcium hydroxide. Hydrogen sulphide forms no precipitate.

Neutral or ammoniacal solutions of arsenites form a precipitate with calcium solutions. (Distinction from barium.)

Ammoniacal solutions of calcium salts are precipitated by arsenic acid as $CaNH_4AsO_4$. (Distinction from strontium after the addition of sulphuric acid. (Bloxom, C. N., 1886: 54, 16.)

Crystalline Reactions. — Dilute sulphuric acid will produce clusters of long slender needles from solutions of calcium. Dilute solutions should be allowed to stand for crystallization to proceed, which begins around the margin of the drop. If barium, lead or strontium are also present their amorphous precipitates would mask the calcium sulphate. The preparation should be heated and the mother liquor decanted. From this characteristic needles, $CaSO_4.2H_2O$ will be formed. Trivalent chlorides injure the reaction. (See page 133.)

Soluble carbonates form small rhombs of calcium carbonate.

Oxalic acid forms crystals appearing as very small octahedra, unaffected by the presence of the chlorides of trivalent elements (aluminum, iron, chromium).

A large excess of potassium ferrocyanide will form small squares ($K_2CaFe(CN)_6.H_2O$). If barium is present large rhombohedrons will be formed. There is but little tendency for this reagent to precipitate strontium.

Potassium chromate will precipitate calcium from solutions that are not too dilute. The dichromate does not produce a precipitate.

If strontium must be separated from calcium, the solution should be made slightly alkaline with ammonium hydroxide before adding the dichromate. Under these conditions strontium chromate will precipitate.

Strontium

Chemical Reactions.—Ammonium hydroxide does not precipitate strontium from solutions. Fixed alkalies will cause precipitation of the hydroxide if the solution is not too dilute. The alkali carbonates form strontium carbonate from solutions, and even the sulphate is transposed into the carbonate on heating. (Distinction from barium.)

Strontium sulphate is almost insoluble in solutions of ammonium sulphate. (Separation from calcium.)

Alkaline arsenates fail to precipitate strontium from solutions of the sulphate. (Distinction from calcium.)

Detection.—The spectrum of strontium consists of six bands in the red, one orange and one blue. The chloride is easily volatile in the flame of the Bunsen burner.

Strontium sulphate can be recrystallized from hot sulphuric acid in the form of rhombs and crosses.

Tetragonal crystals appearing as octahedra can be obtained by precipitating strontium salts with oxalic acid in the presence of a trace of nitric acid. (See page 150.)

Barium

Solubility.—It is soluble in acids with the evolution of hydrogen. The oxide is soluble in water, forming the hydroxide which is basic.

The iodate, fluosilicate, sulphate, phosphate, sulphite se-

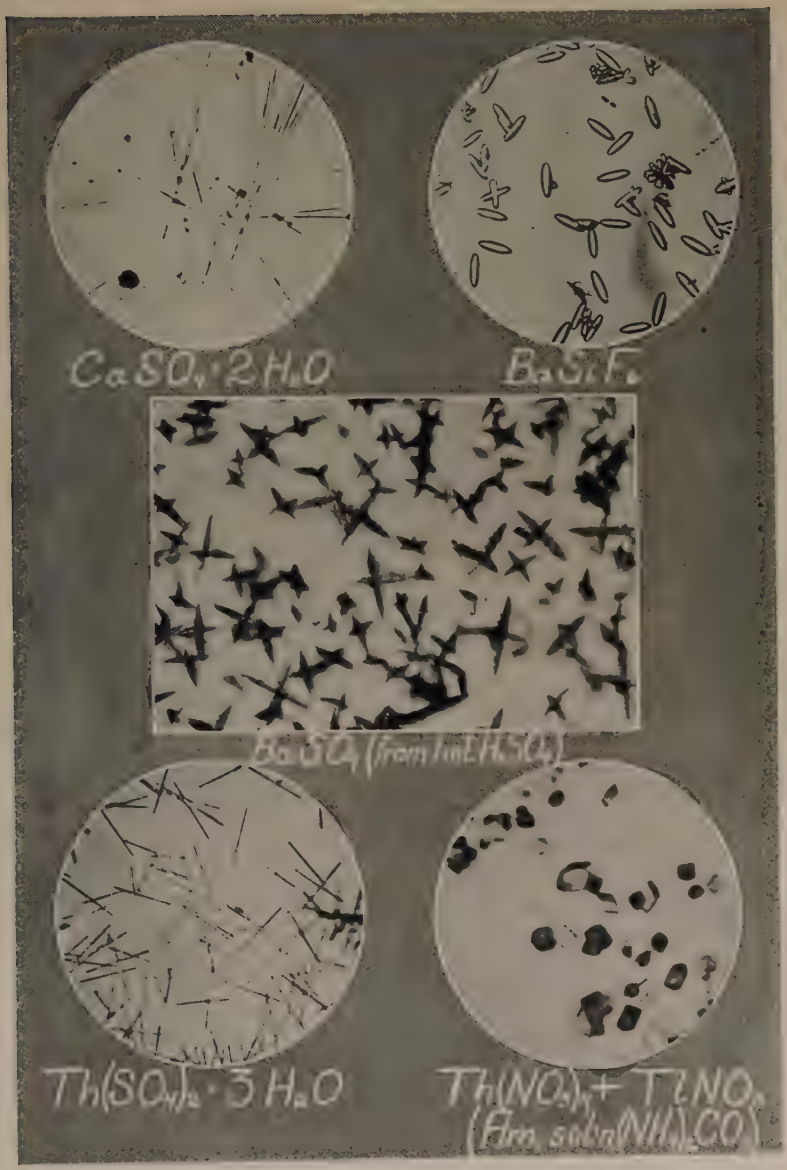

$CaSO_4 \cdot 2H_2O$
$BaSiF_6$
$BaSO_4$ (from H_2SO_4)
$Th(SO_4)_2 \cdot 3H_2O$
$Th(NO_3)_4 + TlNO_3$
(Hrn. soln $(NH_4)_2CO_3$)

Fig. 26.

lenate, oxalate and chromate are insoluble in water. The chloride is soluble with difficulty in concentrated hydrochloric acid. The chloride and nitrate are insoluble in alcohol.

Detection.—Alkali carbonates precipitate barium carbonate incompletely in the presence of ammonium salts.

Soluble sulphates precipitate barium sulphate from all solutions of barium salts. This precipitate can be recrystallized from hot sulphuric acid in the form of delicate crosses.

Sodium iodate forms difficultly soluble $Ba(IO_3)_2$ with solutions of barium salts. (Distinction from other members of alkaline earth group.)

Fluosilic acid gives a characteristic crystalline precipitate with solutions of barium salts. The precipitate is not soluble in alcohol. (Distinction from calcium and strontium.)

Soluble chromates and dichromates will precipitate barium chromate from solutions slightly acid with acetic acid. (Distinction from calcium and strontium.)

Volatile salts of barium give a green color to the flames of the Bunsen burner, and show green bands in the spectroscope.

Tartar emetic will precipitate rhombs or six sided plates of $(Ba(SbO)C_8H_4O_{12}.2H_2O$ from solutions of barium salts. The preparation should be acidified with acetic acid and alkalies and alkaline earths must be avoided. Time must be allowed for sufficient concentration to take place by evaporation if dilute solutions are employed. (See page 101.)

DIVISION B (ALUM GROUP)

Aluminum, chromium, iron (valence 3), indium and gallium.

Aluminum

Chemical Reactions.—Aluminum dissolves readily in hydrochloric acid and in fixed alkalies. It is attacked more slowly by sulphuric and nitric acids.

From solutions containing aluminum fixed alkalies precipitate aluminum hydroxide, insoluble in water but soluble in an excess of the reagent. The presence of certain organic acids, such as citric or tartaric acids, prevents the complete precipitation of aluminum hydroxide, due to the formation of a soluble double salt.

An insoluble basic acetate may be formed by heating to boiling a solution of aluminum salts with sodium acetate. The addition of a little sodium carbonate aids the reaction.

Aluminum is precipitated from solutions as the hydroxide by phenylhydrazine, soluble sulphides, soluble thiosulphates* and sulphites. In this way aluminum can be separated from iron. Congo red produces a blood-red color with aluminum hydroxide.

Crystalline Tests.— The best crystalline test for aluminum is with cesium sulphate. The alums formed with rubidium and potassium are more soluble than the cesium compound and too much time is required for crystallization.

The aluminum compound should be converted to the sulphate by digestion with a drop of sulphuric acid. The residue is then dissolved in water and a grain of cesium chloride or sulphate is added. From solutions containing more than 1% of aluminum the crystallization is too rapid, resulting in the formation of dendrites. The crystallization is slow when the percentage of aluminum falls below .2%, or when large quantities of alkali salts are present. The crystals are colorless octahedra, and are beautifully formed. ($Cs_2SO_4.Al_2(SO_4)_3.24H_2O.$) (See page 141.)

Ammonium fluoride also produces octahedra from solutions of aluminum if the reagent is added in excess. Sodium and ferric salts should be absent. This reaction is more serviceable than the formation of cesium alum if the solutions are very dilute. A large excess of aluminum results in the formation of small rods. The characteristic octahedra of the double fluoride ($AlF_3.3NH_4F$) are smaller than the cesium alum crystals, but are very well developed.

*Iron is not precipitated by sodium sulphite or sodium thiosulphate.

Chromium

Chemical Reactions.—Chromium burns to the oxide Cr_2O_3 when heated in air at a temperature of about 250°. The metal is soluble in hydrochloric or dilute sulphuric acids, but is not in nitric. It is scarcely soluble in concentrated sulphuric. Both chlorine and bromine convert the metal to the corresponding halides.

Alkali sulphides and hydroxides will precipitate chromium hydroxide which is soluble in acids or exceess of the alkali. The latter will convert the hydroxide to a chromite which can be oxidized to a chromate by such oxidizing agents as chlorine or hydrogen peroxide.

Chromium trioxide (CrO_3) is formed by the addition of potassium dichromate to concentrated sulphuric acid. The needles are reddish brown.

Detection.—If chromium is present as a chromate or dichromate an excellent crystalline test is by means of silver nitrate in the presence of a trace of nitric acid. (See Silver.) If chromium is to be detected in iron, the metal is reduced to a powder, oxidized with nitric acid, dried and fused on platinum with sodium carbonate and potassium nitrate. The "cake" is then ground with water and the clear solution containing the chromate is concentrated and tested with silver nitrate. The resulting silver chromate crystals are large, and range in color from an orange to a deep red. (Behrens.)

The formation of the double sulphate of chromium and cesium requirees more time than for the preparation of cesium alum. The chromium compound to be tested should be first converted to chromium sulphate. This can be done by precipitating the chromium first as the hydroxide by means of ammonia and then adding just sufficient sulphuric acid to dissolve the precipitate. The preparation should be concentrated almost to dryness, and then a grain of cesium sulphate added. The crystals of cesium chrome alum are colorless when thin but become a delicate violet as they develop thickness. Organic and mineral acids should be avoided.

OTHER ALUMS

Ferric sulphate will form with cesium sulphate ferric alum crystals resembling those of aluminum. The preparation, however, has to be quite concentrated, and considerable care employed. As the crystals develop thickness a decided yellow color can be noticed.

INDIUM, GALLIUM and THALLIUM also form alums. Their absence can be verified by means of the spectroscope. These alums are far more difficult to crystallize than cesium aluminum sulphate, and do not materially interfere with the detection of aluminum or even chromium.

DIVISION C

Sodium

CHEMICAL REACTIONS.—Most of the compounds of sodium are readily soluble in water. Sodium pyroantimonate (see Antimony) and sodium fluosilicate are exceptions to the rule, and even these are slightly soluble. It forms double salts that are more soluble than the analogous compounds of potassium.

DETECTION.—From concentrated solutions it can be precipitated by chloroplatinic acid as Na_2PtCl_6, forming red prisms and needles. (Distinction from ammonia, potassium, rubidium and cesium.) [1]

The precipitate formed with bismuth sulphate is quite characteristic. The sodium compound should be first converted into the sulphate, and evaporated to dryness. To a drop of bismuth sulphate solution a fragment of this dry residue is then added. Slender needles and prisms form almost immediately around the edge of the drop and later rod-like needles form in the center. These give parallel extinction. Free mineral acids retard the crystallization of the sodium bismuth sulphate $3Na_2SO_4 . 2Bi_2(SO_4)_3$. Potassium forms six sided plates with the same reagent.

Sodium can be detected in dry residues by means of uranyl acetate. The sodium solution is evaporated to dryness on

a glass slide. A drop of uranyl acetate solution is placed by the dry residue and a small stream is led by the point of the stirring rod directly across the film of sodium compound. The tetrahedra of sodium uranyl acetate $NaC_2H_3O_2.UO_2(C_2H_3O_2)_2$ are faintly yellow by reflected and black by transmitted light. (See page 141.)

Sodium can be traced even in the presence of potassium by this reagent on account of the high solubility of the double acetate of potassium and uranium. Potassium, rubidium, cesium and ammonium give slender tetragonal prisms which do not appear until the preparation goes almost to dryness.

If magnesium is present a triple acetate ($NaC_2H_3O_2.Mg(C_2H_3O_2)_2.(UO_2(C_2H_3O_2)_2.9H_2O$) may appear in the form of curving triangles, rhombs and octahedra. The magnesium must be in excess.

The formation of sodium pyroantimonate has been described under "Antimony" and the formation of sodium silicofluoride under "Silicon."

Potassium

Reactions.—Like sodium, the hydroxide of potassium is a strong base, and precipitates as hydroxides all of the metals except cesium, rubidium and lithium.

Chloroplatinic acid added to solutions of potassium precipitates yellow octahedra of K_2PtCl_6, provided the solution of potassium is not too dilute. If such is the case time must be allowed for the drop to approach dryness. A trace of HCl is beneficial. (See Platinum.)

Perchloric acid forms a difficultly soluble perchlorate with potassium salts. Potassium perchlorate ($KClO_4$) crystals are orthorhombic, highly refractive and clear cut. They have the property of absorbing permanganates, becoming a rose red. (See page 141.)

Bismuth sulphate added to solutions of potassium sulphate forms a double salt $3K_2SO_4.Bi_2(SO_4)_3$ crystallizing in the form of circular disks and hexagonal plates (Distinction from sodium). (See page 141.)

Potassium picrate has a low solubility and can be made to crystallize in clusters of characteristic needles if the solution is not too dilute.

Potassium compounds give a violet coloration to the flame of the Bunsen burner.

Ammonium

Unfortunately most of the tests for potassium can also be applied to "ammonium." If the ammonium radical is thought to be present it is best to volatilize the ammonia in a distilling crucible, and fix the vapors in a hanging drop of dilute hydrochloric acid. The ammonium compound is placed in the small crucible, sodium hydroxide is added and a cover glass with a hanging drop of the dilute acid on the under side is pressed down on the top of the crucible. The preparation is then carefully warmed. When all of the ammonia has been volatilized, the hanging drop is tested for the ammonium radical by means of chloroplatinic acid, the crystallization being similar to that produced with potassium salts.

"Ammonium" also forms a double sulphate with bismuth which has a crystalline form resembling the potassium compound.

Cesium and Rubidium

Both of these form alums with aluminum solutions. The cesium compound being the less soluble forms the smaller crystals. (See Aluminum.)

Chloroplatinic acid will precipitate both rubidium and cesium chloroplatinate. The cesium compound is formed immediately and the crystals are very small. The rubidium chloroplatinate crystals are larger than those of cesium but smaller than those of potassium.

Both elements give characteristic lines in the spectroscope.

SULPHATE GROUP

Division D

A saturated solution of potassium sulphate will precipitate from solution the following elements in the form of double sulphates. The crystals in most cases are very fine and short needles, collecting in masses which make drawing almost impossible, and attempts at photography useless.

$Ce_2(SO_4)_3 . 3K_2SO_4$	$Nd_2(SO_4)_3 . 3K_2SO_4$
$La_2(SO_4)_3 . 3K_2SO_4$	$Th(SO_4)_2 . 2K_2SO_4 . 2H_2O$
$Pr_2(SO_4)_3 . 3K_2SO_4 . H_2O$	$Sc_2(SO_4)_3 . 3K_2SO_4$

If there should happen to be present a high concentration of cobalt, nickel, manganese, copper, zinc, magnesium (elements of valence 2) there is a possibility of the formation of monoclinic prismatic crystals of the "pseudo alums," of which the following would be a type:

$$K_2SO_4 . CuSO_4 . 6H_2O$$

Exercises for the Sulphate Group

1. Aluminum.
   (a) To a solution of aluminum sulphate add a fragment of solid cesium sulphate. (Or cesium chloride and a trace of sulphuric acid.) Observe the formation of cesium alum.
   (b) Stain freshly precipitated $Al(OH)_3$ with Congo red.

2. Chromium. To a solution of chromium (valence 3) add solid cesium chloride and trace of sulphuric acid and allow the preparation to concentrate in a dessicator. Allow the crystals to become sufficiently thick to give a violet tint. Cesium sulphate gives better results than cesium chloride and sulphuric acid.

   Oxidize a chromous salt to a chromate with sodium peroxide. Acidify with nitric acid and then add a drop silver nitrate. Observe the red crystals of silver chromate and bichromate.

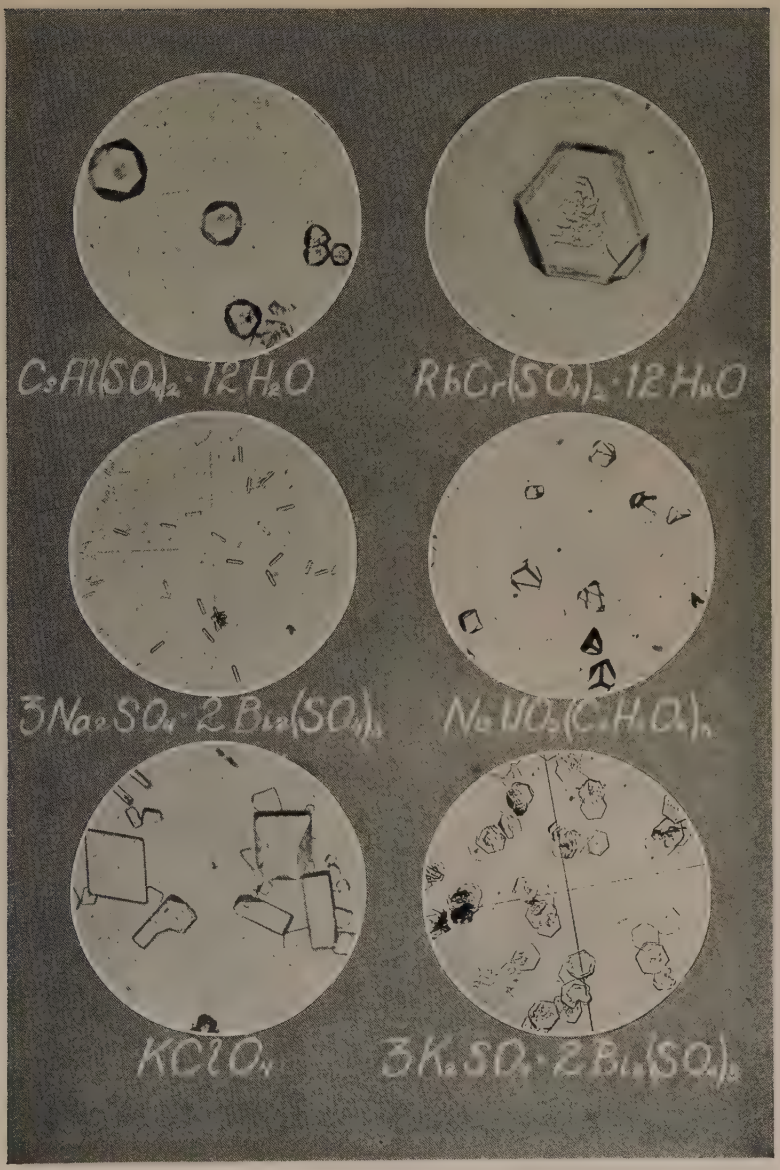

$C_3Al(SO_4)_2 \cdot 12H_2O$
$RbCr(SO_4)_2 \cdot 12H_2O$
$3Na_2SO_4 \cdot 2Bi_2(SO_4)_3$
$NaUO_2(C_2H_3O_2)_3$
$KClO_4$
$3K_2SO_4 \cdot 2Bi_2(SO_4)_3$

Fig. 27.

3. IRON. Repeat Exercise 1, using a solution of ferric sulphate. The solution should be allowed to concentrate. The crystals of cesium ferric alum are yellow.

4. CALCIUM. To a solution of calcium salts add a trace of dilute sulphuric acid and allow concentration to take place. Note the formation of bundles of slender needles. ($CaSO_4.2H_2O$). (See page 133.)

5. BARIUM. To a dilute solution of barium chloride add a trace of sulphuric acid. Digest the precipitate in a corner of the slide in the acid and allow to cool. If the preparation becomes too dry moisten gradually by breathing upon the slide. Note the delicate crosses of barium sulphate. (See page 133.)

6. STRONTIUM. Repeat Exercise 5, using a solution of strontium. Observe that similar crosses are formed, also rhombs.

7. Observe the crystallization of strontium oxalate. (See page 150.)

8. SODIUM. Evaporate a solution of sodium acetate on a glass slide. A uniform film should be obtained. With the point of the glass rod draw across this film a solution of uranyl acetate. Observe the formation of small yellow tetrahedra, which may develop a cubic habit. (See page 141.)

9. From a dilute solution of sodium salts precipitate the double sulphate of sodium and bismuth by the addition of a trace of nitric acid and a small amount of bismuth sulphate. (See page 141.)

10. Repeat Exercise 9, using a potassium salt in place of sodium. (Absence of ammonium salts.)

11. Observe the crystallization of potassium as the picrate, and also as the perchlorate and chloroplatinate. (See Platinum.)

12. Vaporize some ammonia by treating ammonium compound with NaOH in a distilling crucible. Fix the gas in a hanging drop of dilute HCl and test for ammonia with H_2PtCl_6. Yellow octahedra should be formed similar to K_2PtCl_6.

13. Note the low solubility of cesium and rubidium alums and chloroplatinates. (This is indicated by speed of precipitation and crystal size.)

THE OXALATE GROUP AND TEST LIMITS

		Limits in Micromilligrams (.001 milligram)
BERYLLIUM	With $K_2C_2O_4$	.08
CERIUM	Na_2SO_4	.02
	Na_2CO_3	.05
	$H_2C_2O_4$	.04
	$K_4Fe(CN)_6$	.1
NEODYMIUM	With Na_2SO_4	.07
	With Na_2CO_3	.1
PRASEODYMIUM	With $H_2C_2O_4$	.1
	With $K_4Fe(CN)_6$	.15
LANTHANUM	With Na_2SO_4	.04
	With Na_2CO_3	.06
	With Oxalic acid	.06
	With $K_4Fe(CN)_6$	.1
MANGANESE	As double phosphate	.3
	With $H_2C_2O_4$	.5
	As MnO_2	.2
RHODIUM	As double nitrite	.09
	As Oxalate	.4

Manganese

Chemical Reactions.—Manganese may have a valence of two, three, four, six and seven. This makes it possible for the element to have many interesting reactions, many of which cannot be taken up in a book of this kind.

The oxide (MnO) is the base from which the stable salts of manganese are formed, and can be obtained by igniting the carbonate, hydroxide or oxalate. Manganese dioxide may be prepared by heating the nitrate to 200°.

Potassium manganate (K_2MnO_4) is the principal salt of manganic acid. Manganates have a green color which in solution gradually become red due to the formation of permanganates.

Fixed alkalies precipitate from solutions of manganous salts, manganous hydroxide, which gradually turns brown on exposure to oxygen of the air.

Ammonium hydroxide only partially precipitates manganous salts, the presence of the ammonium salts causing the formation of a soluble complex salt.

The halogen acids reduce the higher oxides of manganese to manganous salts, halogen gases being evolved.

Detection.—Manganese can be precipitated from solution by caustic alkalies and the resulting hydroxide heated with nitric acid and PbO_2. The red color developed due to the permanganate formed is an indication of manganese.

Sodium bismuthate can be used as a substitute for lead dioxide. After stirring in a small quantity of the reagent a pink color will develop, accompanied with a brown deposit of oxide of manganese. Dissolve this precipitate in the least possible amount of sodium thiosulphate, add another drop of dilute nitric acid and a few more fragments of sodium bismuthate. The purple color of the permanganate formed can be absorbed by crystals of potassium perchlorate if a trace of potassium chlorate is added and then a drop of perchloric acid.

Potassium chromate will produce from solutions of manganous salts clusters of yellowish brown needles. The drop

should contain only a trace of nitric acid, and the concentration of the manganese should not be too low. Lead, silver, bismuth, etc., should be absent.

The best crystalline test is with oxalic acid or with primary potassium oxalate. A film of the potassium oxalate is prepared on a glass slide and a drop of the solution to be tested is placed close by. With the sharp point of the glass sampling rod a narrow channel is made by leading the drop into the dry film of the oxalate. Thin prisms are formed, pointed at the ends and have a tendency to form clusters of three or six. They give parallel extinction and polarize well. Free mineral acids should not be present.

Glucinum (Beryllium)

Chemical Reactions.—Fixed alkalies precipitate glucinum hydroxide which is soluble in excess of the reagent. Ammonium sulphide precipitates glucinum as the hydroxide. Ammonium carbonate precipitates the glucinum as a carbonate that is soluble in excess. (Separation from aluminum.)

Detection.—The best crystalline test for glucinum is with potassium oxalate. A small amount of potassium oxalate will precipitate small crosses of beryllium oxalate. An excess of the reagent will cause the formation of highly refractive prisms of the monoclinic system ($BeC_2O_4.K_2C_2O_4$). There is a tendency to twin. If a large excess of the reagent is added clusters of pale leaves, pointed at each end, will be formed accompanied by pale rhombs. Crystallization may be started by introducing a solid fragment of potassium oxalate into the test drop. (See page 146.)

If mercuric chloride is also added to the preparation the drop becomes filled with long prisms giving beautiful colors between crossed nicols.

Ammonium salts should be absent when testing for beryllium with potassium oxalate.

Uranyl acetate will form pale yellow rhombs with solu-

Fig. 28.

tions of beryllium acetate in the presence of a small amount of sodium acetate. The crystals are large (200μ). Too much sodium acetate results in the formation of the double acetate of sodium and uranium. (Method of Streng.)

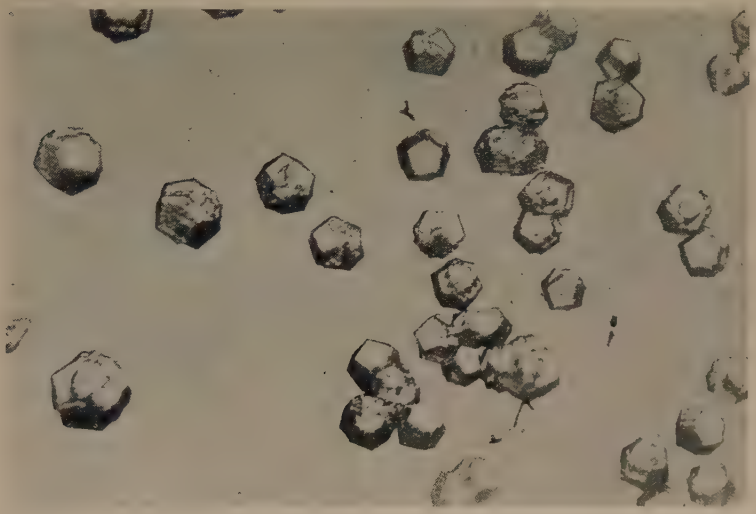


Fig. 29. Dodecahedrons of cerous formate. (Herndon.)

Cerium

Chemical Reactions.—Cerous solutions are colorless. Ceric salts form yellow solutions which are decolorized by sulphurous acid forming cerous salts.

The fixed alkali hydroxides and ammonium sulphide will precipitate cerous hydroxide which is slowly oxidized to the ceric condition by absorbed oxygen, and is insoluble in excess of the reagent. (Distinction from Al & Be.)

Alkali carbonates will precipitate cerous carbonate which is soluble in excess of the reagent.

A saturated solution of potassium sulphate will precipitate cerium as a double sulphate ($K_3Ce(SO_4)_3$. The crystals are very small needles.

A crystalline precipitate is formed by oxalic acid with

cerous salts and is less soluble in hot than in cold water. Sometimes the powdery precipitate first formed will produce not only the slender needles and tiny crosses but larger plates.

Haushofer recommends precipitating cerium with soluble formates. It is difficult to obtain the dodecahedra that he describes. They are small and are soon covered with many fine needles in such a manner that the crystals more closely resemble spheres.

Lanthanum

The Element.—Lanthanum may be incompletely separated from cerium compounds by precipitating them both as the oxalate and igniting them at red heat. The resulting ceric oxide is not soluble in dilute nitric acid, but the oxide of lanthanum easily dissolves.

The metal is prepared from the chloride by electrolysis, or by ignition with sodium. It reacts with water slowly when cold but violently when hot. The oxide is soluble in water and gives the solution an alkaline reaction with litmus. Ammonium sulphide and alkali hydroxides precipitate lanthanum hydroxide $La(OH)_3$, insoluble in excess of the reagent.

Detection.—Potassium sulphate (saturated solutions) will precipitate a double sulphate of lanthanum and potassium. This is not easily distinguished from other double sulphates formed in the same manner. If thallous sulphate is employed six sided plates are produced.

Sodium carbonate will first produce a gelatinous precipitate which will change to "prickly knobs" after standing for some time.

Oxalic acid will produce needles and pointed rhombs usually grouped in bundles. Time must be allowed for the first granular precipitate to become crystalline.

Potassium ferrocyanide (traces) will form a double compound crystallizing in colorless hexagonal plates and

rhombs. Ammonium succinate will produce both fine and coarse prisms of lanthanum succinate.

Exercises for the Oxalate Group

1. Manganese. To a solution of manganese add a trace of acetic acid and a drop of oxalic acid. Observe the twinned slender crystals with basal angles of 60°. (See page 150.)

2. Cadmium. Observe the crystallization of cadmium oxalate. These truncated prisms should not be mistaken for those of manganese. (See page 121.)

3. Zirconium. To a solution of zirconium sulphate add potassium acid oxalate. Note the formation of rhombs of the double oxalate of potassium and zirconium.

4. Prepare precipitates of the oxalates of zinc, nickel, calcium, barium and strontium. (Note that large amounts of such elements would mask the crystallization of manganese.)

5. Lanthanum. To a solution of lanthanum add a drop of oxalic acid and observe the crystallization. (See page 146.)

6. Add a solution of sodium carbonate to a lanthanum salt (dilute solution). Allow the preparation to stand for thirty minutes and then observe the "prickly knobs" that have formed.

7. Repeat Exercise 5, substituting a cerium salt for the lanthanum.

8. Repeat Exercise 5, substituting a salt of neodymium or praseodymium for the cerium.

9. Observe the precipitate obtained by sodium or potassium sulphate with salts of the cerium group of rare earths. (Avoid an excess of strong acids.)

Fig. 30.

THALLOUS NITRATE GROUP AND TEST LIMITS

		Limits in Micro-milligrams (.001 milligram)
GOLD	With $SnCl_2$	2.0
	With $Tl(NO_3)$	6.0
IODINE	As TlI	.17
	As AgI	.17
	As PdI_2	.1
	As K_2PtI_6	.2
	As HgI_2	.2
	With starch	.17
MOLYBDENUM	As phosphomolybdate	.1
	As Tl_2MoO_4	.033
PALLADIUM	Precipitation with KI & NH_3	.1
	With HCl & $TlNO_3$	.2
	With NH_4CNS & $TlNO_3$	.07
	As $N_2H_6PdCl_2$	.2
TUNGSTEN	As WO_3	1.6
	As phosphotungstate	.12
	As Thallous tungstate	.08
THORIUM	As sulphate	30.00
	With oxalic acid	.1
	With $(NH_4)_2CO_3$ & $TlNO_3$	.05
URANIUM	With sodium acetate	.6
	With am. carbonate & $TlNO_3$	.1
VANADIUM	As NH_4VO_3	.3
	With $AgNO_3$	.07
	With $TlNO_3$	.07
CHLORINE	$TlNO_3$	.1
	$AgNO_3$	.05
	As Tl_2PtCl_6	.004
	As K_2PtCl_6	.5

Gold

The Element.—Gold is not soluble in the common acids. It is attacked by oxidizing agents such as aqua regia, chlorine or bromine. It is also soluble in potassium cyanide and in molten zinc. It amalgamates readily with mercury. The extraction of gold from its ores is based upon these well known properties. Metallic gold crystallizing in the cubic system can be found in quartz.

Compounds.—Gold can exist in compounds in both the monovalent and trivalent condition. When dissolved in the presence of such oxidizing agents as aqua regia it is found in the trivalent condition, and is soluble. When auric chloride is heated to 180° aurous chloride is formed, which is an insoluble white powder, behaving like copper in the cuprous condition. Trivalent gold behaves like aluminum, the hydroxide reacting with bases to form aurates such as $NaAuO_2$.

Separation.—Hydrogen sulphide precipitates from solution both auric and aurous sulphides, which are soluble in ammonium polysulphide. In separating these from arsenic, antimony and tin the mixture is fused with sodium carbonate and potassium nitrate. The mixture is heated with water and filtered. The aresnic is soluble. The residue is reduced to the metallic form by the addition of zinc and hydrochloric acid. Boiling the mixture with concentrated hydrochloric acid dissolves the tin. The residue is heated with nitric acid and tartaric acid to remove the antimony, which is soluble. Gold and platinum will remain. These may be dissolved by aqua regia and the gold precipitated by oxalic acid. The platinum will be in solution.

Exercises With Gold

1. To a solution containing gold add a trace of mineral acid. Then add ferrous sulphate or oxalic acid. Examine the yellow powder by transmitted and also reflected light.

2. Dissolve the precipitated gold in aqua regia. To a very dilute drop of this solution add a drop of stannous chloride. This forms the "purple of Cassius."

3. To a drop of a gold solution add a drop of a mixture of stannous and stannic chlorides. Where the two drops touch a red granular precipitate will form.

4. Cesium chloride added to a gold solution causes the formation of yellow squares and rectangles. (The cesium chloride added should be in the solid form.) (See page 101.)

5. Rubidium chloride added to a gold coin solution results in the formation of prisms which have truncated ends.

6. To a gold solution add ammonium thiocyanate in excess. Pale red rosettes will form, freely soluble in ammonium hydroxide or hot ammonium thiocyanate. This solution will precipitate zinc and cobalt in the same manner as ammonium mercuric thiocyanate. The zinc salt is yellow, the cobalt a sea green. (Method of Behrens.)

7. To a drop of gold solution free of HCl add a grain of thallous nitrate. Long yellow needles will sprout from the crystals of thallous nitrate. Heat must be cautiously applied to avoid reduction of the gold and oxidation of the thallium. (Method of Behrens.) (See page 101.)

(Mercuric chloride will give colorless needles with thallous nitrate.)

Molybdenum

(Valence 2, 3, 4 & 6)

Chemical Reactions.—The oxide (MoO_3) dissolves in acids to form soluble salts. The nitrate is kept in solution with dilute nitric acid, the sulphate and chloride are soluble. The oxide reacts with alkalies to form molybdates, which are soluble in water. These water solutions will precipitate

all other metals as insoluble molybdates, and are decomposed by acids forming the oxide which dissolves in excess of the acid.

Solutions of di, tri, and tetra valent molybdenum are precipitated from solutions by alkali hydroxide and carbonates, forming hydroxides which oxidize in air to a blue molybdenum molybdate. Solutions of molybdates acidified with HCl become red on the addition of KCNS and metallic zinc. The red color is not destroyed by phosphoric acid. (Difference from ferric iron.)

A crystalline precipitate is obtained with thallous nitrate and molybdate solutions. The crystals are smaller than those produced with tungsten, but the thin plates are very bright and clearly cut. A slight excess of caustic alkali should be present when the grain of thallous nitrate is added. The crystals do not recrystallize well from hot water, only a crust being formed. (See page 159.)

Tungsten

Chemical Reactions.—The dioxide (WO_2) is prepared by decomposing WCl_4 with water. The higher oxide (WO_3) is prepared by ignition of the metal or the lower oxides. By digesting certain decomposable compounds in concentrated HCl it can also be formed. It is a yellow powder insoluble in water and acids. The blue oxides are those lying between WO_2 and WO_3.

The metal is soluble slowly in nitric acid, aqua regia, and alkalies. Hydrochloric acid and sulphuric attack it but slightly. The dioxide is soluble in hot HCl or H_2SO_4, giving a red color, which can also be obtained with KOH.

By fusion of WO_3 with alkalies soluble tungstates are formed, which are precipitated by the addition of excess acid. Under these conditions the white, hydrated tungstic acid would be found in the "Chloride Group." No metal of this group could be present with tungsten except lead or thallium, because the fixed alkali which is keeping the tung-

sten in solution would precipitate silver and mercury. The hydrated acid becomes yellow WO_3 on boiling.

Detection.—Solutions of WO_3 give a blue color when treated with hydrochloric acid and zinc, due to the formation of lower oxides.

Potassium ferrocyanide in acid solution will produce a red color with solutions of tungstates.

Alkali tungstates will precipitate barium, silver, mercury, calcium and lead from solutions of their salts, forming insoluble tungstates.

A crystalline precipitate (Tl_2WO_4), composed of large iridescent six sided plates and stars can be obtained from solutions of tungstates by means of thallous nitrate. The solution should contain a slight excess of alkali and the thallous nitrate added in the solid form. (See page 159.)

Thorium

The Element.—The chief sources of thorium are thorite, monazite and thorianite. The mineral can be digested with sulphuric acid and the sulphate extracted with cold water. On heating this solution to boiling an impure sulphate of thorium can be obtained. From sulphuric acid solutions thorium can also be precipitated as the oxalate by means of oxalic acid.

Chemical Reactions.—The chloride, nitrate and sulphate of thorium are soluble. Thorium compounds form a soluble double oxalate with ammonium oxalate, from which solution excess hydrochloric acid will precipitate the thorium compound. (Distinction from zirconium.)

Alkali hydroxides precipitate thorium hydroxide, insoluble in excess of the reagent. Alkali carbonates precipitate thorium from solution as the carbonate, which is soluble in excess of the reagent but is reprecipitated on heating.

Oxalic acid precipitates thorium oxalate, insoluble in excess of the reagent. If ammonium oxalate, however, is used

as a precipitating agent the precipitate first formed redissolves.

A saturated solution of potassium sulphate added to a solution of thorium salts will produce a double sulphate of thorium and potassium. $Th(SO_4)_2.4K_2SO_4.2H_2O$.

Potassium fluoride added to a solution of thorium may produce a double fluoride ($xKF.yThF_4$).

Crystalline Tests.—Behrens suggested forming crystals of thorium sulphate ($Th(SO_4)_4.3H_2O$) by means of heat. On the corner of a glass slide he placed a cover glass and on this a drop of the solution to be tested for thorium. The drop is heated and the crust around the edge pushed in by means of a platinum wire. If the solution is not too dilute the drop will very shortly become filled with slender needles. (See page 133.)

They can be distinguished from calcium sulphate by adding ammonium hydroxide and ammonium carbonate in which the thorium compound is soluble.

A more sensitive test is with thallous nitrate. The thorium compound is dissolved in an ammoniacal solution of ammonium carbonate and a fragment of thallous nitrate added. The small crystals are in the form of colorless rhombs. Uranium gives *yellow* rhombs under the same conditions, but zirconium, beryllium, and yttrium do not give reactions of this kind. (See page 133.)

Uranium

Chemical Reactions.—Uranium forms two classes of salts, URANOUS and URANYL, which with oxidizing agents somewhat resemble ferrous and ferric salts. Solutions of uranous salts are green, uranyl salts are yellow.

Ignition of uranic nitrate forms $UO_2.2UO_3$ which can be converted entirely to the lower oxide (UO_2) by heating with carbon or hydrogen.

The oxide (UO_3) forms always basic salts, such as $UO_2(C_2H_3O_2)_2$ which will be precipitated from solutions by

alkali hydroxides in the form of a yellow powder, insoluble in an excess of the reagent. ($K_2U_2O_7$ typical.)

Detection.—From dilute solutions of uranyl salts potassium ferrocyanide will produce a red precipitate. This will become yellow on the addition of sodium hydroxide. (Distinction from copper.)

Uranium compounds fused in the borax bead give a yellow color in the oxidizing flame and a green color in the reducing flame.

The formation of yellow tetrahedra of the double acetate of sodium and uranyl has been described under sodium. The triple acetate has been described under magnesium. Tests for uranyl can be performed by reversing the procedure.

A delicate test for uranyl is by means of thallous nitrate and ammonium carbonate in a solution alkaline with ammonium hydroxide. Acid solutions of uranyl are first precipitated with ammonium hydroxide and a grain of thallous nitrate is added, then a strong solution of $(NH_4)_2CO_3$. Many short needles are formed on the fragments of the thallous nitrate, and in the open spaces elegantly clear cut rhombs develop, giving a pale yellow color and brilliant polarization. (See page 158.)

The addition of potassium ferrocyanide will convert the double carbonate into reddish grains.

Vanadium

The Element.—The element is prepared from the chloride (VCl_2) by ignition in a current of hydrogen. It is a gray powder which oxidizes rapidly when heated in air forming V_2O_5. The oxide may also be prepared from the ores by fusion with potassium nitrate. The potassium vanadate thus formed is soluble and can be precipitated as lead or barium vanadate. Treatment with sulphuric acid decomposes the vanadate, forming vanadic acid. The preparation is then neutralized with ammonium hydroxide and solid am-

monium chloride added, which precipitates ammonium metavanadate (NH_4VO_3), a crystalline precipitate, insoluble in ammonium chloride. Ignition of this precipitate gives V_2O_5.

Chemical Reactions.—Metallic vanadium is soluble in nitric acid, forming a blue solution. Concentrated sulphuric attacks the metal forming a greenish yellow solution. Dilute sulphuric and hydrochloric acids are without effect.

Vanadic acid forms three series of salts, ortho, meta, and pyro. The alkali vanadates are soluble in water but the ammonium vanadate is almost completely insoluble in ammonium chloride solution. The brown precipitate formed with the alkalies is soluble in excess of the alkali, giving a yellowish-brown color.

Zinc with dilute sulphuric acid will reduce vanadate salts to the divalent condition. The green of the tetravalent vanadium first appears, followed by the greenish blue of the trivalent, and finally the lavender blue of divalent vanadium is observed.

For microscopic work alkaline solutions of vanadic acid are precipitated as ammonium metavanadate by means of ammonium chloride in large excess. The crystals are small pointed needles.

Silver nitrate added to a hot solution of metavanadates strongly acidified with acetic acid will produce orange rods, and clusters of small needles.

Laboratory Exercises

1. Uranium. Precipitate an acid solution of uranyl with ammonium hydroxide. Dissolve this precipitate in ammonium carbonate and add a fragment of thallous nitrate. Observe the formation of pale yellow rhombs. They should polarize strongly.

2. Reverse the test for sodium and make a double acetate of uranyl and sodium. (See Sodium, page 141.)

$Tl_2CO_3 \cdot UO_2CO_3$?
$TlWO_4$
$Tl_2M_0O_4$
NO_3 + Nitron
$MgNH_4PO_4 \cdot 6H_2O$
$MgNH_4PO_4 \cdot H_2O$

Fig. 31.

3. MOLYBDENUM. To a drop of a solution of alkali molybdate add a fragment of thallous nitrate. Allow a few minutes for the drop to concentrate and observe the thin glittering six sided plates of Tl_2MoO_4. Stars may also form.

4. Repeat Exercise 3, substituting tungsten solutions for molybdenum.

5. Prepare crystals of thorium sulphate as described in text.

6. Prepare crystals of the double carbonate of thorium and thallium as described in text.

7. (a) Test a gold solution with solid thallous nitrate. (Avoid HCl.)
   (b) With cesium chloride.

8. Prepare ammonium metavanadate.

9. (a) To a test drop containing palladium nitrate add thallous nitrate. Clusters of needles should form.
   (b) Repeat "a", using in addition NH_4CNS, and recrystallize from hot water. (Large rosettes.)

MISCELLANEOUS GROUP
(As, P, C, Ni, Mg)

		Limits in Micromilligrams (.001 milligram)
ARSENIC	As As_2O_3	.14
	As Am. Ca. Arsenate	.035
	As Arsenomolybdate	.22
CARBON	As $SrCO_3$ or $PbCO_3$	1.0
NICKEL	As $K_2PbNi(NO_2)_6$	.008
	As $NH_4NiPO_4.6H_2O$	.01
MAGNESIUM	As $NH_4MgPO_4.6H_2O$	.0012
PHOSPHORUS	As $NH_4MgPO_4.6H_2O$	.008
	As Am. phos. molybdate	.015

Arsenic

Chemical Reactions.—Solutions of arsenic are precipitated from acid solutions by hydrogen sulphide, forming a yellow precipitate (As_2S_3 or As_2S_5) soluble in yellow ammonium sulphide.

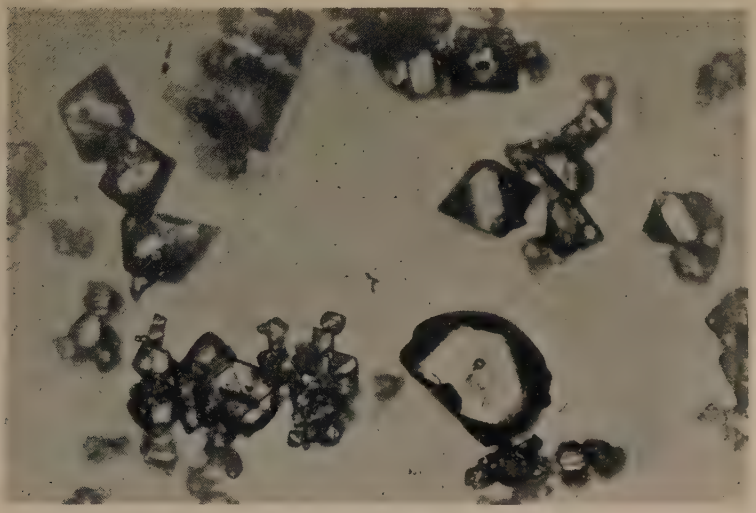


Fig. 32. Crystals of As_2O_3 (sublimed).

In the presence of ammonium chloride and ammonium hydroxide magnesium salts will precipitate white crystalline ammonium magnesium arsenate, crystallizing in ragged X's and in stout prisms.

By careful heating arsenous oxide may be sublimed, forming very beautiful octahedra.

Silver nitrate will precipitate reddish brown crystals of silver arsenate from neutral solutions. They are six sided rhombs. (See Silver.) Silver arsenite precipitated by ammoniacal solutions of silver with water solution of arsenious oxide is yellow.

A delicate test is Marsh's test, which is the formation of an arsenic mirror.

Compounds of arsenic will give a white sublimate when

heated on charcoal before the blowpipe, and the odor of garlic will be noticed.

Ferric salts form insoluble basic arsenites.

Nickel

Chemical Reactions.—Nickelous hydroxide is formed when a fixed alkali hydroxide is added to solutions of nickel salts. The addition of bromine water oxidizes the *nickelous* to nickilic hydroxide, a black precipitate. Alkali carbonates precipitate a green, basic carbonate. Ammonium hydroxide will precipitate the green hydroxide which is soluble in excess of the reagent or ammonium salts. Alkali sulphides precipitate nickel as the black sulphide, almost insoluble in dilute acids, although the presence of free acid prevents precipitation. The phosphate, basic chromate, arsenate, arsenite and cyanides are not soluble. Soluble oxalates slowly precipitate nickel oxalate.

Dimethylglyoxime[1] is a delicate test for nickel. The solution should be slightly alkaline with ammonium hydroxide, and then a drop of the alcoholic solution of the reagent added. A red precipitate forms almost immediately. (Sensitive to 1 part of nickel in 400,000 parts of water.)

A triple nitrite of lead, potassium and nickel can be secured by the addition of potassium nitrite and lead acetate to solutions of nickel in the presence of a trace of acetic acid. The crystals are yellow cubes, and resemble the double nitrite of cobalt and potassium.

Magnesium

Chemical Reactions.—Fixed alkalies will precipitate magnesium from solutions as the hydroxide. Ammonium hydroxide will precipitate magnesium incompletely due to the formation of soluble double salts. Basic carbonates are precipitated by fixed alkaline carbonates, but ammonium car-

[1]One gram of dimethylglyoxime dissolved in 100 c.c. of 98% alcohol.

bonate does not precipitate magnesium due to the formation of a double carbonate. Bicarbonates of the alkalies do not precipitate magnesium carbonate except on boiling, the bicarbonate of magnesium being soluble.

Alkali phosphates precipitate magnesium phosphate, and from very dilute solutions a crystalline precipitate ($MgNH_4PO_4$) can be obtained by the addition of ammonium hydroxide and ammonium chloride. The crystalline precipitate forms slowly and should be stirred. It may occur as irregular crosses or stout prisms, depending upon the concentration and speed of crystallization.

Exercises for the Miscellaneous Group

1. Nickel. To a solution of nickel made slightly alkaline with ammonium hydroxide add a few drops of alcoholic dimethylglyoxime. Examine the preparation for the fine pink crystals.

2. To a solution of nickel add a fragment of lead acetate and an excess of potassium nitrite. The solution should be slightly ammoniacal. Observe the yellow cubes of $K_2PbNi(NO_2)_6$.

3. Magnesium. To a solution of magnesium add a drop of ammonium hydroxide, an excess of ammonium chloride and then an alkali phosphate. Observe the crystallization of magnesium ammonium phosphate in skeleton crosses and prisms. (See page 159.)

4. Arsenic. Repeat Exercise 3, substituting a soluble arsenate for the soluble phosphate. (Observe the similarity of the crystallization of the arsenate and phosphate.)

5. Prepare crystals of silver arsenate. (See Silver.) To obtain large crystals recrystallize the first precipitate from NH_4OH.

6. By careful warming, sublime a small amount of arsenous oxide. Observe the well formed octahedral crystals.

7. Fuse a grain of sulphur with a mixture sodium carbonate and sodium nitrate. Dissolve the mass in a drop of water and test for sulphur as a sulphate with barium or calcium chloride.

IDENTIFICATION OF THE MORE COMMON ACIDS[1]

A solution of silver nitrate added to a concentrated drop of the unknown solution will give either

1. No precipitate except when the preparation approaches Dryness . . . . Group I.
2. A precipitate may be formed which is *colored* by reflected light . . . . Group II.
3. The precipitate which forms is *colorless*, and may be
   (A) Insoluble in HNO_3
   (B) Soluble in HNO_3

Group I

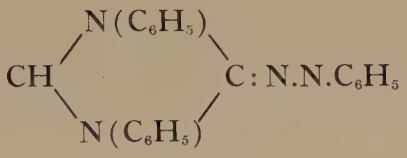
(No precipitate with $AgNO_3$ solution)

Sulphates. To a drop of the solution to be tested add a very small fragment of calcium chloride. Bundles of slender needles indicate the presence of *sulphates*. (See page 133.)

Nitrates. To a drop of the solution to be tested add a drop of acetic acid in which has been dissolved a few crystals of nitron. $C_{19}H_{24}N_2O.HNO_3$ may also be formed by the addition of the acetate of cinchonamine. Nitron gives bundles of slender needles *insoluble in warm water*. The other reagent produces rhombic plates. The nitron compound has the formula, $C_{20}H_{16}N_4.HNO_3$. Nitron is also known as Di-phenyl

[1]Recommended by Dr. E. M. Chamot.

endanilodihydrotriazol, and may be written structurally as follows:



FLUORIDES. The presence of fluorides can be detected by the formation of

1. Sodium silicofluoride. (See page 108.)
2. Barium fluosilicate. (See page 133.)
3. Heating with $KHSO_4$ in a closed tube and observing the etched surface of the interior of the tube. It will appear as a white ring caused by HF attacking the glass.

PERCHLORATES. The addition of KCl to a solution of perchloric acid or soluble perchlorates will cause characteristic crystals of $KClO_4$ to be formed. (See page 141.)

These may be stained pink by the addition of a little potassium permanganate to the preparation.

CHLORATES. If chlorates are suspected to be present convert them to perchlorates by heating with H_2SO_4 several times and expelling the excess acid. Then test for PERCHLORATES.

GROUP II

(The precipitate with silver nitrate is colored by reflected light.)

If

A. REDDISH

Bichromate. Deep red rhombic crystals. Some have one corner cut off. (See page 77.)

Arsenate. Brownish red. (See page 77.)

Ferricyanide. Add a trace of sodium acetate and then a solution of benzidine hydrochloride. Blue prisms and stars appear.

If

B. Yellow

Arsenite. Make the Marsh Test.

Phosphate. Test with $MgCl_2$ & $NH_4OH + NH_4Cl$. (See page 159.)

Iodide (faint yellow). Insoluble in ammonium hydroxide. Test another drop with lead nitrate and examine the preparation for six sided yellow plates.

Iodate (faint yellow). Add a trace of dilute sulphuric acid, then a few grains of potato starch, then a crystal of sodium sulphite—blue. Morphine sulphate may be used instead of the sulphite.

C. If Violet

Permanganate, or manganate.

D. If Black

Sulphide. To a small portion in a distilling apparatus add a trace of mineral acid. Allow the fumes to attack a hanging drop containing a solution of sodium nitro-prusside—purple.

Arsenate will appear black if the crystals are thick. (See page 77.)

Group III

(The precipitate with nitric acid is colorless.)

Division A

The colorless precipitate is insoluble in nitric acid.

Chlorides. (a) The silver salt is soluble in ammonium hydroxide.

(b) Lead nitrate added to a new drop of the preparation gives forked crystals, or prisms. (See page 81.)

(c) Thallous nitrate added to a new drop gives crosses.

Bromides. To a new drop add a trace of sulphuric acid. Warm gently and then cool. Add a fragment of potato starch and a crystal of ammonium persulphate. The free bromine will turn the starch yellow. The preparation must be examined QUICKLY. Potassium permanganate added to the acid solution will liberate the bromine and color the starch a bright yellow immediately.

Iodides. (a) The silver precipitate is insoluble in ammonium hydroxide. The bromide and chloride are both soluble.

(b) The addition of lead nitrate gives yellow six sided plates. (See page 81.)

(c) The preparation when treated as described above for bromides will give a deep blue color.

Ferrocyanide. To a drop of the solution add a trace of $FeCl_3$. A deep blue color indicates ferrocyanides.

Sulphocyanates. To a drop of the solution add $FeCl_3$ solution. A deep red indicates sulphocyanates.

Mixed Halides. Chlorides can be identified in presence of bromides and iodides by means of platinic sulphate and addition of a cesium salt, resulting in the formation of Cs_2PtCl_6.

Division B

(The white precipitate dissolves in HNO_3)

ACETATES. Prepare a dry film of sodium chloride on a slide. Near this place a drop of the solution to be tested and add to the drop a small amount of Uranium nitrate.

(a) Draw a line of this solution across the dry film and examine along the edges for yellow tetrahedra of sodium uranyl acetate. (Neutral preparation. (See page 141.)

(b) From concentrated solutions copper nitrate will give blue dichroic monoclinic crystals.

(c) The precipitate from silver nitrate shows pearly crystals.

BORATES. (a) Solutions of borates will turn tumeric paper reddish. (In acid solution.)

(b) Prepare crystals of potassium fluoborate. (See page 113.)

CARBONATES. (a) Note any effervescence when acid is added.

(b) Expose a hanging drop of lead acetate to the vapors as in the test for ammonia, and then examine for crystals of lead carbonate.

CYANATES. To a concentrated solution add cobalt acetate crystal. A blue color will indicate cyanates. (Remember, a solution of mercuric salts in solution with thiocyanates of the alkali metals will also give a blue color. The crystals of this compound are easily distinguished, however, from those of cyanates.)

IODATES. Test as described under Group II, Div. B.

NITRITES. (a) Masses of needles with silver nitrate. Green in clusters.

(b) To the solution add a trace of dilute sulphuric acid, a fragment of KI and a trace of potato starch. The starch will appear blue.

(c) Try out the triple nitrite reaction. (See page 83.)

OXALATES. Strontium nitrate added to a neutral preparation will give crystals of strontium oxalate. Nitric acid is helpful. (See page 150.)

SULPHATES. Barium chloride gives a white amorphous precipitate. Calcium chloride gives bundles of slender colorless needles.

SULPHITES. To a drop of the unknown, add a crystal of potassium iodate, a trace of dilute sulphuric acid and then a little potato starch. The preparation will become blue.

TARTRATES. Calcium acetate added will develop large and well defined crystals. Avoid mineral acids.

THIOSULPHATES. These will bleach iodine solution.

SUCCINATES. Give colorless crosses with $AgNO_3$.
Give colorless rhombs with lead acetate.

CHAPTER V

Common Alkaloids

Literature.—Most of the alkaloids described here are those that can be found at the corner drug store. To attempt to give crystalline tests for all of the known alkaloids and their derivatives would require a separate volume such as that published by Stephenson,[1] in which the microchemical reactions of sixty-four of the alkaloids are described and one hundred and sixty-two photomicrographs given.

Wormley in his "Microchemistry of Poisons" described in considerable detail the effect of common alkaloids on the body and the procedure involved in their recovery and detection. The descriptions are accompanied with very fine etchings.

If the student desires additional information concerning the structure or extraction of alkaloids the very complete volume by "Henry" is to be recommended.

A number of alkaloids are described by Behrens-Kley[2] in "Organic Mikrochemische Analyse." There are numerous drawings and many refractive indices given.

Reagents

Wagner's Reagent—

Iodine	10 grams
Potassium iodide	50 grams
Water	1000 c. c.

Kraut's Reagent—

A—Bismuth nitrate 80 grams in 200 c.c. HNO_3 Sp. gr. 1.18

B—Potassium iodide 272 grams. Dissolve this in a little water and add to A.

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[1]Stephenson: Microchemical Tests for Alkaloids. Lippincott, Phila.
[2]Behrens-Kley: Organische Mikrochemische Analyse. Vose, Leipsic.

Zinc-chlor-iodide—

Zinc chloride	100 grams
Water	60 c.c.
Potassium iodide	20 grams
Iodine	6 grams

Mayer's Reagent—

Sufficient potassium iodide is added to a 1% solution of mercuric chloride to redissolve the precipitate first formed.

Millon's Reagent—

A given amount of mercury is dissolved in approximately the same weight of concentrated nitric acid. The solution is diluted with an equal volume of water.

Phosphotungstic acid—

Phosphotungstic acid is prepared by dissolving about 70 parts of sodium phosphotungstate in 500 parts of water and acidifying with nitric acid.

Phosphomolybdic acid—

Concentrated nitric acid	1 part
Water	10 parts
Sodium phosphomolybdate	1 part

Marme's Reagent—

Cadmium Iodide	30 grams
Potassium iodide	60 grams
Distilled water	180 c.c.

An Outline for the Identification of Common Alkaloids[1]

Group I—Solid Alkaloid gives no color change with cold conc. H_2SO_4.

[1]This outline is by no means complete. It is a convenient outline for the common alkaloids and can be enlarged if necessary to meet the analyst's requirements

A Division (Colored in Nitric Acid)

1. Heroin, Dionine, Nicotine.....Reagent: $HgCl_2$
2. Morphine, Codeine (faintly colored). Reagent: Marme's Reagent
3. Berberine.....Reagent: Chromic Acid

B Division (Colorless in Sulphuric acid and in Nitric acid)

1. Atropin, Caffein, Cocaine, Opianyl, Quinidine, Quinine, Strychnine.....Reagent: $AuCl_3$
2. Betaine, Conine hydrochloride. Reagent: Phosphotungstic Acid
3. Cinchonidin.....Reagent: Platinic Chloride
4. Gelsemine, Cystin.....Reagent: Ether or HCL

GROUP II.

A (Color change when heated with Sulphuric acid)

1. Narcotine (fine needles in KOH), Veratine (Amorphous in KOH), Delphinine (slightly colored in cold H_2SO_4 also), Codeine.

GROUP III.

A (Colored in Cold Sulphuric Acid)

1. Conine, Jervine, Solanine, Brucine, Narcein.

GROUP I

DIV. A (COLORED IN NITRIC ACID)
NICOTINE

THE ALKALOID.— Nicotine is an oily liquid with an odor resembling that of tobacco. When pure it is colorless but on exposure to air becomes brownish. It begins to distill at about 146°, boils at 243.5°C, and is strongly alkaline.

SOLUBILITY.—It is soluble in turpentine, ether, alcohol, chloroform and in water. For extraction of nicotine chloroform is usually used. Most of the salts of nicotine are soluble in water but insoluble in ether. They have no odor and part of the nicotine is lost when they are concentrated by evaporation.

Identification.—The alkaloid will give a reddish liquid when treated with nitric acid; with sulphuric it becomes brown on heating.

A double chloride is formed when salts of nicotine react with chloroplatinic acid. Ortigosa gave the compound the formula $C_{10}H_{14}.2HCl.PtCl_4$. The presence of free hydrochloric acid causes crystallization almost immediately. The crystals are soluble in excess of free nicotine. The yellow crystals are entirely different from those produced by the same reagent with the alkalies. (See page 179.)

Mercuric chloride will precipitate crystals of a nicotine compound provided the solution is not too dilute. The crystals polarize well. Dilute solutions should be allowed to stand in order to develop large groups, because the limit is only .0004 grains (Wormley). They will be easily soluble in acetic acid. (Distinction from strychnine.)

Auric chloride or bromine in hydrobromic acid will also produce precipitates with solutions of nicotine. The precipitates are not usually crystalline but non-appearance would indicate absence of nicotine, as the limit of the reaction is about .00002 grains (Wormley).

Wormley describes a crystalline precipitate (limit .000025 grains) made by picric acid. The crystallization resembles that of $AuCl_3$.

Dionine (Ethyl-morphine)

Ethyl morphine chloride ($C_{17}H_{18}O_2N(OC_2H_5).HCl.2H_2O$) is an alkaloid prepared from morphine. It melts at about 123°C without decomposition.

Chemical Reactions.—A 1% solution of the alkaloid warmed with 10 c.c.'s of sulphuric acid and a drop of ferric chloride will turn first green and then blue. If a drop of nitric acid is added the solution becomes a deep red.

Potassium ferricyanide and ferric chloride will give the green and blue color characteristic of morphine.

Wagner's reagent will give clusters of rods in solutions of .5% of the alkaloid.

Mercuric chloride gives an amorphous precipitate with 2% solutions of dionine. Clusters of plates are formed from solutions containing as little as .5%. (See page 182.)

Precipitates approaching the amorphous condition are obtained with zinc-chlor-iodide and also with Mayer's reagent.

Heroine (Diacetyl morphine)

Heroine is a white crystalline powder with a faintly bitter taste. It is almost insoluble in water but is soluble in dilute acids. The drug has been officially removed from the market.

Chloroplatinic acid produces rosettes of needles as the preparation approaches dryness. From dilute solutions the crystallization is slow.

Picric acid gives a heavy amorphous precipitate. Small spheres predominate.

Potassium cyanide forms large plates from solutions containing .5% of heroine. They give good polarization colors.

Mercuric chloride produces clusters of needles sometimes appearing like knife blades. (See page 182.)

Sodium carbonate produces an amorphous precipitate which slowly changes to crystalline plates. It polarizes well.

No good crystalline tests for heroine were obtained from concentrations greater than one-half of one per cent.

Morphine

The Alkaloid.— Morphine melts at about 253°. If heated too rapidly it decomposes. It crystallizes from alcoholic solution in rhombic plates or needles containing one molecule of water. This is slowly lost at 75°C. The neutral salt has five molecules of water.

At 25° one part of morphine is soluble in 15.3 parts of water. It is less soluble in alcohol and almost insoluble in ether and chloroform. From the alcoholic solution the crystals are small but from aqueous solution they may grow quite long. From aqueous solution the sulphate is orthorhombic, crystallizing in rectangular prisms.

Colors.—An orange color is produced with solid morphine and nitric acid. This gradually fades into a yellow. There is no color change with cold sulphuric but on heating it becomes a purplish brown. With potassium dichromate and sulphuric acid it is at first colorless but later becomes green. With potassium iodate and sulphuric acid a brown is produced, and with iodine in potassium iodine a reddish brown amorphous precipitate with .00002 grain. With platinic chloride the delicacy is only one-half as great. Prussian blue is obtained when a few drops of ferric chloride is added to a solution containing morphine and potassium ferricyanide. (Sensitive to 1 part of morphine in 50,000.)

Crystalline Reactions.—Marme's reagent will produce very satisfactory crystals if the concentration of the morphine is greater than one part in a thousand. They occur as clusters of slender needles.

Ammonium carbonate or sodium carbonate will produce prisms of considerable size if the solution is not too dilute. Thin crystals appear as colorless rectangles. The dilution should not exceed 1 : 250 for good results. (See page 176.)

From more concentrated solutions (1 : 60) mercuric chloride will form rosettes quite rapidly.

From concentrated solutions of salts of morphine potassium iodide will precipitate crystalline needles which will grow to considerable length as the drop approaches dryness. At least .01 grain of the alkaloid should be present.

Caustic alkalies will precipitate colorless prisms, many having forked ends. The fixed alkali should not be too strong as the crystals are soluble in excess. If the dilution of the alkaloid is as much as .001 of a grain only a granular deposit is obtained.

Yellow rectangles are obtained if potassium chromate is added to neutral solutions of morphine salts. If the dilution is greater than .0005 grain the crystallization is not very satisfactory.

Codeine (Methyl ester of morphine)

The Alkaloid.—Codeine crystallizes from aqueous solution with one molecule of water. Anhydrous codeine can

Morphine + KI
Morphine + (NH4)2CO3
Morphine + K2Cr2O7
Codeine + KCNS
Morphine SO4 + HgCl2
Codeine + KI

Fig. 33.

be obtained from solutions in benzol or ether. According to Wormley pure codeine is soluble in water 1 : 128. Absolute ether dissolves one part of the alkaloid in 55 of the liquid. Chloroform is a better solvent, dissolving one part in 21.5 parts of the fluid. Codeine is also soluble in alcohol and to some extent in caustic alkalies. It neutralizes dilute acids and forms crystallizable salts. With cold concentrated sulphuric acid there is no color change but on heating in a water bath a purple color appears. Codeine gives little or no color change with nitric acid and less with hydrochloric. Aqueous solutions of codeine have a bitter taste and give an alkaline reaction.

Most salts of codeine are soluble in water and alcohol. Ether and chloroform dissolve them with great difficulty or not at all. Crystals of codeine sulphate separate from alcoholic solution with an axial ratio a : b : c : : .288 : 1 : .419. The base sometimes appears without the brachydome causing the crystals to have square ends. The sulphate has a melting point near 278°C.

Microchemical Reactions.—A crystalline deposit is obtained with a solution of iodine in potassium iodide when codeine is present to the extent of .01 grain. The crystals are soluble in alcohol from which they can be recrystallized into plates giving many colors with polarized light. At greater dilution yellow deposits are obtained and even when only .00002 grain is present a distinct turbidity can be detected.

Potassium thiocyanate gives clusters of colorless crystals immediately if the preparation is stirred and the concentration of the codeine is as much as .01 grain. At greater dilutions of the alkaloid several minutes must elapse before the formation of these deposits begins. (See page 176.)

Fixed alkalies precipitate codeine as an amorphous precipitate. This pure codeine is soluble in acids, from which solution it can be made to crystallize into long, thick orthorhombic prisms.

Mercuric chloride will produce crystal aggregates, prisms and needles if the solutions are not too dilute.

Potassium dichromate will produce bright red crystals with strong solutions of codeine. Potassium chromate will produce yellow plates and rectangles under the same conditions.

Potassium iodide produces tufts of needles from concentrated solutions of codeine. (See page 176.)

Amorphous precipitates are thrown down by both auric chloride and platinic chloride. With the former a cloudiness can be noticed at a concentration of .00002 grain, with the latter .0002 grain is the limit.

With potassium ferricyanide and ferric chloride codeine does not give an immediate color change. Morphine does, on warming.

Marme's reagent precipitates codeine compounds from solutions as dilute as 1 : 2000. At greater concentrations clusters of crystalline plates will be formed.

Wagner's reagent will produce brown rosettes from solutions of medium concentration. From dilute solutions amorphous precipitates are formed.

Div. B

(Colorless in cold H_2SO_4 or HNO_3)

Cocaine (from Erythroxylim coca)

$C_{17}H_{21}NO_4$ (Methyl ester of benzoyl ecgonin)

The Powdered Leaves.—The Peruvian coca powder consists of green fragments of epidermal tissue having polygonal cells and elliptical stomata usually carrying two neighboring cells. Calcium oxalate crystals occur in monoclinic prisms about .006 mm. in diameter. They may or may not occur singly.

The Alkaloid.—The crystals of the alkaloid are colorless and are of the monoclinic system. They may have four or six sides. They have an axial ratio

$$a : b : c :: .8432 : 1 : 1.032; \beta\ 73^\circ\ 50',$$

are tabular on the base, and elongated on the b axis which

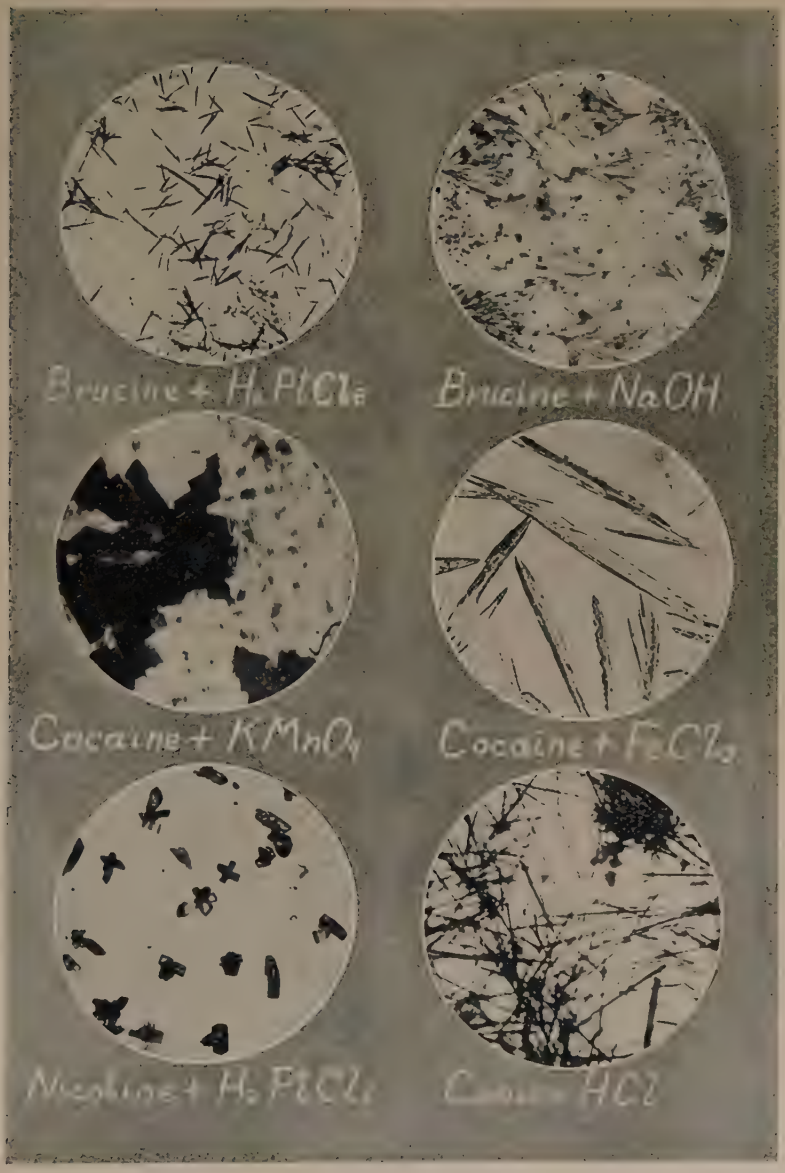
Brucine + H_2PtCl_6
Brucine + NaOH
Cocaine + $KMnO_4$
Cocaine + $FeCl_3$
Nicotine + H_2PtCl_6
Caffeine + HCl

Fig. 34.

is the direction of least refractive index. Sometimes interference figures can be obtained. Their M. P. is about 97°. They have a bitter taste but no odor, and are soluble in water, in common organic solvents, such as alcohol, ether and chloroform. Of these chloroform is the most efficient.

Detection.—D. Scherbatschew suggests placing 3 drops of the suspected substance in aqueous solution on a glass slide, and adding respectively one drop each of 10% solution of ammonium and potassium hydroxides, and last a saturated solution of sodium bicarbonate.

Stovaine and holocane give precipitates with all 3 reagents. Beta-eucaine gives only a slight precipitate with KOH and none with the other two.

Nirvavine gives a ppt. with NH_4OH, a slight one with KOH, but none with sodium bicarbonate. Alypine gives a precipitate with NH_4OH and KOH but not with the other two. Cocaine and tropacocaine are identified by Hankins' test. (Potassium permanganate.)

Crystalline Reactions.—Chloroplatinic acid gives a characteristic precipitate with solutions of cocaine up to a dilution of something like 1 : 3500. They are yellow feathery clusters.

The crystals obtained with ferric chloride are large blades and spear points. This test, however, is not very sensitive.

Auric chloride first produces an amorphous precipitate which in dilute solutions will change over into fern-like rods of crystals growing at right angles to each other. Rosettes form in more concentrated solutions. With gold chloride

Alpha eucaine gives branching twig-like crystals. Stovaine gives large crystals resembling cocaine chloroplatinate, with smaller branches.

Beta-eucaine	amorphous
Acoine	amorphous
Holocaine	amorphous
Euphthalmine	no precipitate

Potassium permanganate will produce purple-colored plates if added to a solution of cocaine that is not too dilute. The preparation should be stirred, and only a small amount of the reagent added. The test works well at dilution up to 1:500. The presence of other alkaloids may make this test useless.

Crystalline precipitates can be produced also by palladious chloride; by potassium dichromate; potassium cyanide; and fixed alkalies. These tests however are not very sensitive.

Strychnine

The Alkaloid.—Strychnine forms less than one-half of one per cent by weight of "nux vomica." According to Regnault it has the formula $C_{21}H_{22}N_2O_2$ when anhydrous. It is a virulent poison, the ordinary medicinal dose being usually not over one-sixteenth of a grain. It has a bitter taste, burns with a yellowish flame and when heat is cautiously applied fuses to a brownish mass subliming at 174°C.

It is basic and unites with acids to form salts, one of the most common of which is the sulphate. This is usually found with several molecules of water. This salt crystallizes in four-sided prisms belonging to the tragonal system. The nitrate and acetate are silky needles.

Solubility.—The salts of strychnine are soluble in water. The presence of free acid increases this solubility. The pure alkaloid is readily soluble in chloroform, less in alcohol and only slightly soluble in water.

Color Reactions.—In the presence of concentrated sulphuric acid and potassium dichromate strychnine gives first a violet color changing to a purple, later to a cherry,[1] and finally to an orange. Violet colors are also obtained if either potassium iodate or ammonium vanadate is substituted for potassium dichromate.

[1]The presence of Bruceine interferes with many color reactions for strychnine, particularly, when the ratio of strychnine to Bruceine is less than 10 to 1. Morphine also interferes.

Fig. 35.

Crystalline Reactions.—Fixed caustic alkalies will produce with .01 grain of strychnine an amorphous precipitate which soon changes to clusters of fine needles. If the solution is increased to .0002 grain satisfactory crystals can be obtained provided a short time is allowed and the preparation stirred. The crystals are easily soluble in acids.

Potassium thiocyanate produces with strychnine solutions stout prisms which have a tendency to cluster, radiating from a common center. They are insoluble in excess of the reagent and resist the action of acids to some extent. The test is sensitive to .0002 grain of the alkaloid, provided some minutes elapse before the preparation is examined. Stirring also aids the crystallization. Nicholson and Abel claim these crystals to have the composition

$$C_{21}H_{22}N_2O_2 . HCNS.$$

Potassium iodide produces similar crystals and the reaction has about the same sensitiveness.

Potassium dichromate produces from strong solutions of strychnine "bush-like" crystals. From more dilute solutions octahedral crystals appear accompanied by plates. The limit of the reaction is almost twice that of potassium thiocyanate. The yellow deposit is soluble in strong nitric acid. With concentrated sulphuric acid the preparation becomes a deep blue.

Auric chloride produces "bush-like" yellow crystals from solutions more concentrated than .001 grain. If .00002 grain is present a turbidity only is obtained. (See page 182.)

Platinic chloride produces with solutions of strychnine an amorphous precipitate of strychnine chloroplatinate. Wormley gives its composition as $2C_{21}H_{22}N_2O_2 . HCl . PtCl_4$. It is a pale yellow and becomes crystalline on standing. From dilute solutions the crystals require longer time to form but can be relied upon to produce a satisfactory test with .0001 grain of the alkaloid. (See page 182.)

Mercuric chloride will precipitate an amorphous mass of the double chloride of strychnine and mercury if the dilution does not exceed .002 grain. The crystals radiate from a central nucleus and in a short time the amorphous mass

becomes largely crystalline. The solution should be neutral.

Potassium ferrocyanide will also precipitate an amorphous deposit which becomes crystalline on standing. The solution should be neutral and at least .002 grain of the alkaloid should be present.

Iodine in potassium iodide (aqueous solution) will give a reddish brown amorphous precipitate which slowly becomes crystalline. The presence of .0001 grain is sufficient to produce a turbidity.

Picric acid forms large curved rosettes.

Wagner's reagent precipitates strychnine even from very dilute solutions. The crystals are in the form of rods.

Atropine (Belladonna)

The Alkaloid.—Atropine is found in the leaves, berries and roots of the "Deadly Nightshade." Analysis by Planta gave the alkaloid the composition, $C_{17}H_{23}NO_3$. The pure solid is white, consisting of acicular needles which may be sublimed. It has a bitter taste, is slightly soluble in water, but more readily in alcohol, chloroform and ether. The salts, however, are more soluble in water.

Chemical Reactions.—Atropine is an active base, neutralizing even the most active acids. It dissolves in sulphuric or nitric acids without change of color. If potassium dichromate crystals are added to the sulphuric acid solution a green color is produced due to the formation of chromium sesquioxide. If alcoholic KOH is added to the nitric[1] acid solution a violet color is produced. Apoatropine is produced by warming the nitric acid solution of the alkaloid. Hydrolysis yields tropin and tropic acid.

Crystalline Reactions.—Auric chloride will precipitate a light yellow precipitate, $C_{17}H_{23}NO_3.HCl.AuCl_3$. This in a short time will become crystalline if the dilution does not exceed 1:5000.

[1]Dr. Vitali states that with over 60 alkaloids examined with this reagent only daturine and atropine responded. Wormley claims hyoscyamine and duboisine also react. The reaction is sensitive up to a dilution of 1:50,000.

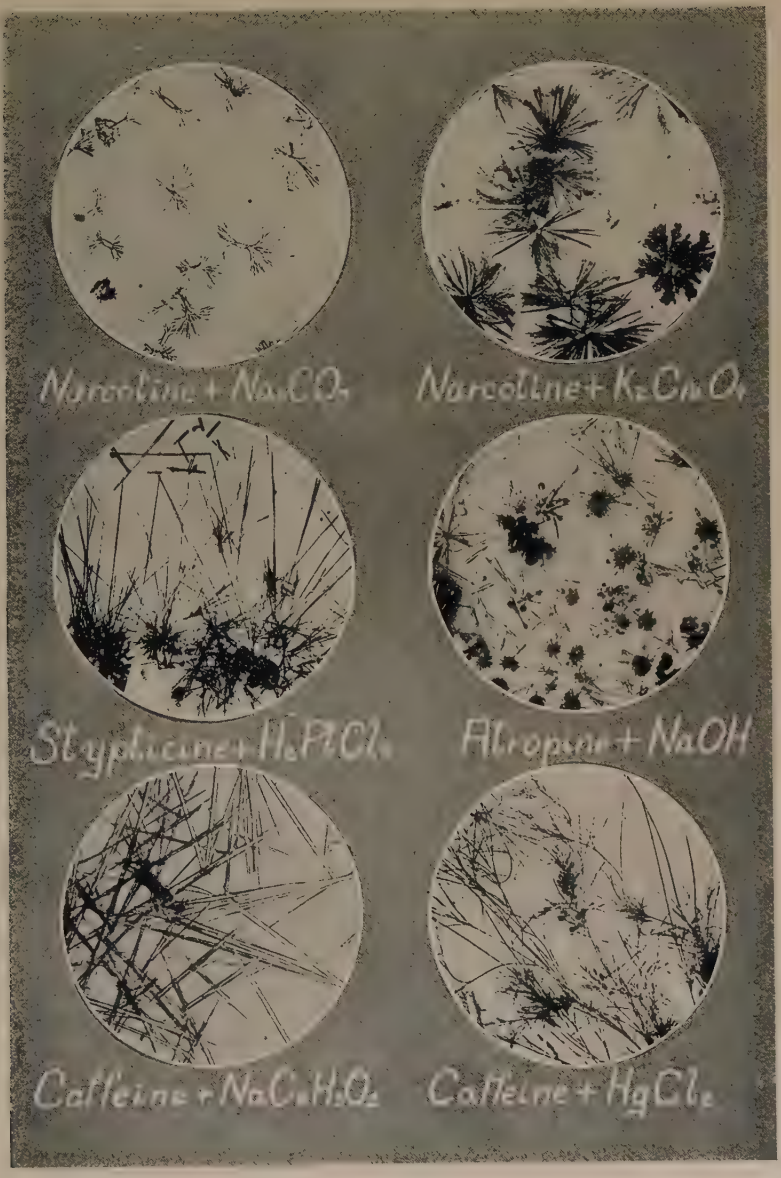
Narcotine + Na_2CO_3
Narcotine + $K_2Cr_2O_7$
Strychnine + H_2PtCl_6
Atropin + NaOH
Caffeine + $NaC_6H_5O_2$
Caffeine + $HgCl_2$

Fig. 36.

Alcoholic picric acid will produce plates, often grouped in clusters with solutions of this alkaloid. The preparation should be stirred and the dilution should not exceed 1:5000.

Caustic alkalies will precipitate rosettes of needles from strong solutions of atropine salts. Solutions more dilute than 1% fail to give a precipitate. The solution should be permitted to stand for a short time so that the amorphous precipitate first formed can become crystalline.

Wagner's reagent forms small rods and plates from solutions up to a dilution of 1:10,000.

Quinine

$(C_{20}H_{24}O_2N_2 . 3H_2O)$

The Alkaloid.—Quinine is obtained from the bark of the cinchona and is usually found on the market as a sulphate. The alkaloid can be obtained by adding sodium hydroxide or ammonium hydroxide to a solution of its salts.

It may be crystallized from alcoholic solution in the form of silky needles. If care is used they can be sublimed. It has no odor, but has a bitter taste.

It is very soluble in ether, chloroform, and benzene. One part of the alkaloid will dissolve in two parts of boiling alcohol and six parts of the cold. Nine hundred parts of boiling water will dissolve one part of the alkaloid. At a temperature of 15°C, 1960 parts of water will be required.

Detection.—Quinine and its salts are distinguished from all other alkaloids except quinidine and quinicine by the emerald green color obtained when their solutions are treated with chlorine and then ammonium hydroxide. This turns to a white or violet on the addition of considerable dilute acid.

If the solution is not too dilute a crystalline precipitate can be obtained with sodium phosphate.

From solutions containing 2% of the alkaloid crystalline precipitates can be obtained by potassium acetate (needles); by potassium chromate (needle rosettes); ammonium thiocyanate (crystalline aggregates).

Caffeine (Trimethylxanthin)

$C_5 H (CH_3)_3 N_4O_2$

The Alkaloid.—The crystals are long prisms showing negative double refraction. They are soluble in water, alcohol and the more common organic solvents. Nitric acid gives a yellow color which becomes red on the addition of ammonium hydroxide. The alkaloid may be sublimed.

Chemical Reactions.—The alkaloid may be precipitated as large needles from acid solutions by means of sodium acetate. (See page 185.)

Mercuric chloride will also precipitate fine needles and long prisms from solutions that are not too dilute. Free hydrochloric acid is injurious. The crystalline precipitate polarizes well. (See page 185.)

Kraut's reagent precipitates small reddish rosettes. This precipitate is at first amorphous, and if the solution is dilute the crystals are very small.

The precipitate formed with auric chloride or platinic chloride forms rather slowly.

Group II

(Color change when heated with conc. H_2SO_4)

Narcotine

The Alkaloid.—The alkaloid can be obtained from the water insoluble part of opium by digesting in acetic acid and then precipitating with ammonium hydroxide. The purified alkaloid can be obtained by digesting this in a hot alcoholic solution with animal charcoal and recrystallizing.—(Gregory.) The crystals are colorless rhombic needles with little taste. They fuse at about 115° and volatilize at 154°. The solutions of this alkaloid are more bitter than morphine.

Solubilities.—According to Wormley narcotine is soluble less than one part in 20,000 at ordinary temperature in pure water. In absolute ether it is soluble one part in 208, and in chloroform and alcohol it is readily soluble. It can be separated from morphine by means of the former sol-

vent. Morphine is also soluble in diluted acetic acid, while narcotine is not. Narcotine like morphine can be precipitated from solutions by means of caustic alkalies.

Color Reactions.— A yellow color is produced by concentrated sulphuric acid with the alkaloid. The addition of potassium nitrate to this solution gives a red color. Hot sulphuric acid gives a purple color, nitric produces a yellow, and sulphovanadic acid produces a red.

Crystalline Reactions.— Alkalies and alkali carbonates precipitate narcotine from solution first as an amorphous deposit which changes on standing into crystalline tufts. If only a trace of the reagent is used it is possible to detect .0025% of the alkaloid. An excess of the reagent is destructive. (See page 185.)

Potassium acetate is not so sensitive a reagent as the alkalies, but very beautiful crystals will appear after a few minutes from the first amorphous precipitate. Free acids will dissolve the crystals. These clusters of prisms are characteristic and their presence is a good indication of narcotine.

Potassium chromate is equally as sensitive as potassium acetate. The yellow precipitate is at first amorphous and changes in a few minutes to crystalline clusters. Stirring hastens the crystallization.

Potassium thiocyanate is a useful reagent for the detection of narcotine as it does not easily under ordinary conditions form crystalline precipitates with *morphine*. It will detect .005% of narcotine. The crystals resemble those formed with the alkalies. It is soluble, however, not only in mineral acids but also acetic.

Auric chloride produces a bright yellow amorphous precipitate, potassium ferrocyanide a white, and picric acid a yellow precipitate from .001% of narcotine. Bromine in hydrobromic acid will give a cloudiness with .00001 grain of the alkaloid in one grain of water.

Cotarnine (Stypticin)

$C_{12}H_{14}O_3NCl.H_2O$ (The chloride)

Wöhler prepared this alkaloid from narcotine by oxidizing with manganese dioxide in the presence of sulphuric acid.

It can also be oxidized with nitric acid, or the narcotine can be hydrolized by boiling with water. The chloride is a yellow crystalline powder that is slightly deliquescent. It is soluble in water and alcohol. It decomposes when heated over the Bunsen burner becoming first a liquid and finally a charred mass. The aqueous solution gives no reaction with litmus.

Identification.—The crystals melt at about 143°. A concentration of 1:50 parts of water gives a brown precipitate of cotarnine periodide on the addition of N/10 iodine. A solution containing 5% of the alkaloid gives a white precipitate with 15% NaOH.

From dilute solutions chloroplatinic acid will precipitate almost immediately masses of long slender needles which arrange themselves in clusters. (See page 185.)

If fragments of mercuric chloride are added to solutions of "stypticin" clusters of needles will almost immediately sprout from the edges of the fragments. Individual needles are larger than those produced with platinic chloride. The solution of the alkaloid should not be too dilute.

Group III
(Colored in Cold Sulphuric Acid)

Narceine
$C_{23}H_{29}NO_9$ (Dr. Anderson)

The Alkaloid.—The mother liquor from the morphine hydrochloride extraction contains several alkaloids, among which is narceine. The addition of ammonium hydroxide precipitates most of the alkaloids but under these conditions narceine remains in solution. This is then filtered and an excess of lead acetate is added which precipitates objectionable materials. The excess lead is removed from the filtrate by means of sulphuric acid. After filtering off this residue of lead sulphate the filtrate is treated with an excess of ammonium hydroxide. After standing for several days the precipitate is dissolved in water and the filtered solution is allowed to cool and crystallize. By boiling the crystals with

water and charcoal a purified product is obtained on recrystallization. The needles liquify at moderate heat and at higher temperatures burn like resin.—(Wormley.)

Narceine is soluble in water 1 : 500 at boiling point. In alcohol it is more soluble. In hot absolute ether one part in 4000 will dissolve. It is approximately half as soluble in chloroform.

Chemical Reactions.—The solid alkaloid treated with concentrated sulphuric acid gives a reddish color which becomes more intense on heating. The addition of potassium dichromate crystals to this acid solution results in the formation of a green color.—(Wormley.)

Nitric acid produces an orange red color with the alkaloid which becomes yellow when solution has taken place.

A yellow crystalline precipitate is obtained by means of a solution of iodine in potassium iodide. The needles will appear after a few minutes even from solutions as dilute as .05%.

Potassium dichromate also gives a crystalline deposit with solutions of narceine. The slender needles are grouped in clusters and are formed almost immediately from solutions as dilute as .2%.

Amorphous precipitates are produced from solutions of narceine by gold chloride, platinic chloride, picric acid and a solution of bromine in hydrobromic acid. The deposit obtained with platinic chloride soon becomes crystalline.

Needles of the hydrochloride separate from solutions as dilute as 1%. The preparation must be warmed if the alkaloid is to be kept in solution.

Brucine

$C_{23}H_{26}N_2O_4$ (Regnault)

(Di-methoxy-strychnine)

In 1819 Pelletier and Caventou discovered brucine in false Angustura bark, which later was found to be bark of the "nux vomica." The bark usually contains less than 1% of the alkaloid. The poisonous effects resemble those

of strychnine but brucine is only about one-tenth that of strychnine. When crystallized from aqueous solution the crystals are either clusters of slender needles or four-sided prisms. The latter form is obtained on slow concentration. Under these conditions the alkaloid has four molecules of water. Like strychnine it has a bitter taste. Its melting point is 105°C and it can be sublimed.

Solubility.— In chloroform or absolute alcohol the alkaloid is quite soluble. It cold water it is soluble one part in 1000, but in hot water its solubility is greatly increased. Nearly all of the salts of brucine are soluble.

Chemical Reactions.— Brucine is decomposed by concentrated nitric acid and forms a red solution. A slight rose color is formed with concentrated sulphuric, and if a trace of nitric is also added the solution becomes a bright red. With sulphuric acid and potassium dichromate an orange color is at first produced, changing to a green. (Distinction from strychnine.) It is less basic than strychnine, and is unacted upon by fixed caustic alkalies.

Crystalline Reactions.— Solutions of fixed caustic alkalies will precipitate brucine from solutions first as an amorphous precipitate. This changes in a short time to bundles of very fine needles and brushes. Ammonia and alkali carbonates will produce results somewhat similar but a large excess of ammonium hydroxide slows up the reaction as the amorphous precipitate is soluble in ammonia. The crystalline is less soluble. Good tests are obtained with .0002 grain of the alkaloid. Acids are injurious. (See page 179.)

Potassium dichromate precipitates brucine from solutions as brucine chromate. It is soluble in sulphuric acid with a brown color and in nitric with a deep red. The characteristic yellow needles and the color reactions in acids distinguishes brucine from all other alkaloids precipitated by potassium dichromate. Wormley was able to detect .001 grain of brucine by allowing the preparation to stand for thirty minutes.

Chloroplatinic acid will precipitate a double chloride of

platinum and Brucine ($2C_{23}H_{26}N_2O_4 . HCl . PtCl_4$.) It is not soluble in acetic acid but the precipitate is destroyed by caustic alkalies. By stirring the preparation and allowing a few minutes to elapse before examining the deposit the irregular yellow needles can be obtained from solutions carrying as little as .00004 grain of the alkaloid. (See page 179.)

If the solution is not too dilute crystalline precipitates can be obtained by mercuric chloride (rosettes); zinc chloride (rods); ammonium thiocyanate (mossy rosettes); Wagner's reagent (rosettes).

Conine

$C_8H_{17}N$ (Hofmann)

The Alkaloid.—Conine is the "active principle" of the common hemlock, and is found most abundantly in the fruit, from which it may be obtained by digesting the ripe fruit with alcohol, distilling off the alcohol, adding potassium hydroxide to the residue and distilling over the alkaloid.—(Dr. Christison.) When pure, conine is a transparent oily liquid with an alkaline reaction. The aqueous solution has an odor of mice. It boils at about 163.5° and distills with water at 100°.

Solubility.—It is soluble in water to the extent of about 1%. An excess of the alkaloid gives the water a milky appearance. It is readily soluble in ether and chloroform. It neutralizes acids, forming odorless salts, most of which are soluble in water but with difficulty in ether. The addition of caustic alkali liberates the alkaloid from its salts.

Identification.—Concentrated HCl added to pure conine gives a pale red increasing in intensity with time, and will deposit rhombic needles (M. P. 54°C) as the drop approaches dryness. The same results are obtained with nitric acid and sulphuric but a longer time is required. The sulphuric acid mixture becomes green on the addition of potassium dichromate crystals.

A drop of the alkaloid exposed to the vapors of hydrochloric acid becomes rapidly crystalline, due to the forma-

tion of needles of the hydrochloride of conine. Dilute solutions of the alkaloid treated with the dilute acid produces like crystals. (See page 179.)

Auric chloride gives a yellow amorphous precipitate insoluble in acetic acid and hydrochloric. The precipitate becomes dark with potassium hydroxide.

Picric acid gives at first a yellow amorphous precipitate, which becomes globules and later large crystals. These are soluble in excess of the alkaloid.

Iodine in potassium iodide gives a reddish brown precipitate when an excess of the reagent is added to solutions of conine. It is soluble in acetic acid. One hundred-thousandth of a grain gives a distinct turbidity.—(Wormley.)

Phosphotungstic acid gives almost instantly a crystalline precipitate of short stout rods even from solutions containing as little as .1% of conine.

Kraut's reagent produces small brown plates from solutions not more dilute than 1:2500.

Barium nitrate produces small rosettes. The solution should be stirred.

Sodium nitroprusside gives a red color, becomes colorless on heating and red again on cooling. This is changed to blue by the addition of aldehydes.

CHAPTER VI

Analysis of Common Textiles

Classification.—Fibers may be conveniently grouped as follows:[1]

1. Animal fibers containing sulphur. (Wool, mohair, and hairs from wild and domestic animals.)
2. Animal fibers containing no sulphur. (The cultivated and wild silks.)
3. Vegetable fibers which give a test for lignin. (Jute, hemp, sisil, vegetable silk, raphia, etc.)
4. Vegetable fibers which give little or no lignin test. (True celluloses.) (Cotton, flax, ramie, etc.)
5. Artificial fibers. (Lustre celluloses.) (Artificial silks.)
6. Mineral fibers. (Spun glass, asbestos, metallic threads.)

GROUP I

Animal Fibers Containing Sulphur

Detection.—Liebermann's reagent distinguishes animal from all other fibers. The reagent is prepared by dissolving one gram of magenta (fuchsin or rosanilin) in 100 c.c. of water. Ammonium hydroxide is added to this until the color is removed. Animal fibers boiled with this solution and then well rinsed will become pink.

One of the simplest ways to detect an animal fiber is to burn it and smell the burning fiber. Animal fibers have quite a disagreeable odor, while the vegetable fibers have not.

Molisch Reaction.—The sample is placed in a test-tube with 1 c.c. of water, 2 drops of alcoholic solution of alpha-napthol and about 1 c.c. of concentrated sulphuric acid. Vegetable fibers will be dissolved and the liquid will become a deep violet in color. Animal fibers will give only a brownish tint.

[1] Dannerth, Methods of Textile Chemistry.

Wools and Hairs.—These are growths occurring on the skins of vertebrates. Their composition is not unlike that of feathers, horn and nails. These growths have roots embedded in the skin which secrete fluids developing the hairs or wools as the case may be. Oil is one of these fluids and gives the hair its softness, pliability and elasticity. The sebaceous glands in the skin secrete a waxy material which offers a protection to the fibers. This is known as wool fat. The central part of the hair is known as the medulla and may contain some pigment. This is covered by the cortical tissue which furnishes strength. The surface is covered with a horny tissue of flattened cells called serrations, whose size and number per linear inch is an indication of the breed of sheep from which the wool came.

Wool Grease.—The source of wool grease is the perspiration flowing from the sudorific glands in the skin. The chief constituent of this grease is one of the higher monatomic alcohols, cholesterol. It is waxy in appearance and will emulsify in water.

Suint.—This is the dried up perspiration consisting of potassium salts of fatty acids. About fifteen per cent of raw wool consists of this material. When this is ignited potassium carbonate is formed, which will amount to about ten per cent of the weight of the raw wool.

The Composition of Wool.—The composition of wool is slightly variable. Among other things it contains a nitrogenous substance called keratin. This holds sulphur in loose combination, and it can therefore be rather easily detected.

Lanuginic acid is the amino acid of keratin. If wool is dissolved in strong barium hydroxide and then carbon dioxide added to precipitate the barium, the nitrogenous compound will be found in the filtrate after the barium carbonate is removed by filtering. A dirty yellow lanuginic acid will be formed if this filtrate is treated with lead acetate and the lead precipitated by hydrogen sulphide and removed by filtration. This acid in aqueous solution will

give colored precipitates with dyes, both acid and basic. This indicates that wool can act as either an acid or a base. The acids in the wool act with basic dyes and the basic material reacts with acids.

Wool is insoluble in dilute acids, is soluble in a hot 5 per cent solution of caustic soda, and is destroyed in concentrated mineral acids. Short immersion in cold sulphuric acid causes it to lose its attraction for acid dyes and increases its attraction for basic dyes.

Chlorination injures wool. It is given a silky scoop by solutions of hypochlorites which cause it to lose its felting qualities, but its attraction for dyes is increased.

Mercerized wool is made by treating it for five minutes at 20°C with a caustic soda solution 80°Tw. The tensile strength is increased about one-third by this treatment, and the wool has a good luster and a silky scoop.

Bleaching of Wool and Hair.— This can be accomplished with hydrogen peroxide. The color can also be removed by potassium permanganate at 120°F. The permanganate can be removed, if an excess is used, by either oxalic acid or sodium bisulphite. Bleaching is often necessary before the serrations on the surface of colored hairs can be counted.

Detection of Sulphur in Hairs.—(a) The sulphate method is often employed particularly when the amount available is very small. The hair or wool as the case may be is heated with sodium carbonate and nitrate of soda in a small combustion tube, or on the corner of a glass slide. A drop of hydrochloric acid is then added and the sulphates formed are precipitated by barium chloride. If the glass slide method is used the crystals of barium sulphate can be observed with a high power of the microscope. If calcium chloride is used instead of barium, slender needles will be formed.

(b) If a sample of wool is dissolved in caustic soda to which a little lead acetate has been added a black precipitate of lead sulphide will be formed.

(c) If the wool is heated with sodium in a small combustion tube and then treated with sodium nitro-prusside in aqueous solution, a violet color will indicate sulphides.

Detection of Nitrogen.—If some wool is heated with sodium in a small combustion tube sodium cyanide will be formed. Boil this with ferrous sulphate and ferric chloride and acidify with hydrochloric acid. The well known compound, "Prussian blue," will appear.

Wools and hairs respond to the general reactions for proteins. Millon's reagent (Aqueous solution of $HgNO_3$) becomes red when warmed with wool or hair. If animal fibers are warmed with a 10 per cent copper sulphate solution and after cooling sodium hydroxide is added, the solution becomes a deep blue. (Biuret reaction.) Wools become yellow when treated with a 50% solution of nitric acid. If wool is boiled with glacial acetic acid, cooled, and then treated with concentrated sulphuric acid, the solution becomes violet. (Adamkiewicz's reaction.)

Varieties.—The scales of coarse wool are horny and are attached firmly to the cortical structure. The scales are from 500 to 1300 per inch. The diameter of coarse wool is about .001 inch. These physical qualities make the wool appear long, hairy, lustrous and light in color. It is the wool of the Lincoln, Leicester, and Cotswold type.

Medium wool has a diameter of about .0008 inch and may vary in length from 3 to 8 inches. The serrations are about 2000 per inch. This class of wool is obtained from the breeds of Southdown, Shropshire, Hampshire, Oxfordshire, Dorsetshire, and also of the Cheviot Hills.

Fine wool is obtained from the Rambouillet sheep of France and the Merino of Europe and Australia. It is non-lustrous, short, crimpy and fine. The diameter is about .0005 inch. The serrations are about 2800 per inch and the length is from 2 to 5 inches.

Shoddy.—This is made from recovered wool and is often mixed with other fibers, such as silk and cotton. Even bamboo fiber has been known to be present in some of the

foreign cloths to the extent of fifty per cent. The appearance of shoddy under the microscope will vary with the variety of fibers going to make up the mixture. ONE OF THE MOST CONVENIENT METHODS EMPLOYED IN THE DETECTION OF SHODDY IS TO OBSERVE THE MANY COLORED FIBERS PRESENT.

QUALITY OF WOOLS.—There are about 5000 hairs per square inch on a sheep and at least eight varieties. The quality of the wool will vary not only with the different breeds of sheep but the wool on an individual will vary in quality depending upon its location. "Hog wool" is a trade name given to the first shearing of a two-year-old sheep. "Wether wool' is gotten from a sheep previously clipped. The eight grades are from the following places:

1. Shoulders and sides. The best wool is found here. It is strong and uniform. It should be fairly free from burrs. It will be soft and long.
2. Back-lower and center. The wool here ranks next to the best.
3. Loin and back. Here the wool is shorter, weaker and probably gritty.
4. Upper part of legs. Burrs will be present here. The wool is of medium length.
5. Upper neck. Burrs will be abundant and the staple irregular.
6. Belly. A poor quality of wool is found here. It is short and weak.
7. Tail. Here the fibers are very short and very coarse.
8. Head, chest and shins. The wool here is short, stiff and straight.

HAIR FIBERS.—A large number of hair fibers are employed in the textile industries. The chief hair fibers are mohair, alpaca, cashmere, cow hair, and camel hair.

MOHAIR.—This hair is very long and fine. It has a silky luster and no curl. It is obtained from the Angora goat. Turkey leads in the production of this fiber, Cape Colony

furnishes almost as much and the United States comes third. In 1902 Turkey produced 8,500,000 pounds. It is used for plushes, felt hats and linings. The fiber is about 18 cm. in length with a diameter about .001 inch. The scales are thin and flat but uniform. A single scale may surround the entire fiber. Under polarized light the fibers may sometimes show a central canal.

CAMEL HAIR.—There are two kinds of hair on the camel. The beard hair is stiff and is used for carpets and blankets. The fine soft hair is used for making Jagar cloth. Both fibers show faintly the presence of scales. The color is usually a dark brown which cannot readily be bleached out. The hair must therefore be dyed a dark color. If a medulla is present in the fiber it often contains dark spots of brown coloring matter which are characteristic.

COW HAIR has a short staple. It is used in blankets, carpets, and in felted goods. The central canal is well defined and occupies about one-fourth of the diameter. The diameter is from 85 to 180 μ. Most of the hair is removed from the hide before the skins are made up into leather. The student should look for the presence of hair roots showing that the fibers were pulled out.

CASHMERE is a very soft fiber used in the making of Indian shawls. As is usual with hair fibers one finds both the coarse beard hairs and the fine down-hairs. The fine cashmere hair has a diameter of 13 μ, while the beard hair has a diameter of about 75 μ. The beard hair has a medulla but the fine hair has none.

Other hairs which are used in the textile trade are alpaca, vicuna, Llama, horse hair, cat hair, rabbit hair.

If an examination of a textile or fur requires search for the presence of a definite kind of hair, it is a good plan to examine with the microscope a specimen of the known fiber and compare the diameter, serrations, and the appearance of the central canal (if any) with the fiber of the unknown.

Animal Fibers Containing No Sulphur

(Cultivated and Wild Silks)

Cocoons.—The most important variety of silk worm is Bombyx mori and the most used food is the leaf of the mulberry. Some care has to be observed each season in the hatching of the new supply of worms, and precautions have to be taken against disease in both the young and older worms.

The worm secretes a double thread which is cemented together by a glue-like substance called sericin as the fibers emerge from the worm. Over one-half of the entire secretion of the worm is FIBROIN which is the chief constituent of silk. The sericin covers this, forming a protective coating. The worm wraps this fiber around itself in one continuous thread varying in length from 300 to 1000 yards.

The composition of the cocoons when sold is approximately

Water	68.2%
Silk	14.3%
Web and veil	.7%
Chrysalis	16.8%

The removal of the silk from the cocoons is accompanied by considerable waste in the form of broken threads, so that only about two-thirds of the silk on the cocoon is available for filaments. The waste is used in spun silk.

When the silk is degummed in a soap solution at 95°C the loss is about 25 per cent in weight. This loss is made up, however, by weighting the silk, sometimes as much as two hundred per cent.

Physical Properties.—Silk will absorb water greedily. Even though it appears dry to the touch it may have as much as 30 per cent of moisture present. Moisture content should therefore be determined on the day of sale. The legal amount permitted is 9.91 per cent.

The strength of the silk is remarkable. Its breaking

strain is approximately one-third that of an iron wire of same diameter.

It is a poor conductor of electricity. This increases the difficulty in manufacture as it is readily electrified by friction.

The density of silk (1) 1.33 raw
(2) 1.25 boiled off

Varieties of Silk Waste.—The silk waste which enters commerce may originate from many sources. The refuse from the raising of the silk worms is known as WATT SILK, and the residue on the cocoon after reeling is called by such names as recotti, galettame, basinetto, etc. Some cocoons are spotted on account of the pupa breaking. This silk is used for floss silk spinning. A waste formed from double cocoons is known as strussa, and that obtained in reeling cocoons is called frisonnets. In addition to these there are a great variety of wild silks converted into waste, and there is the refuse formed in the reeling and spooling. The waste from the tangled and irregularly spun silk on the outside of the cocoon is valuable, as this is very finely spun.

1. **Mulberry Silk.**—The true silk (from Bombyx mori) is not so flat as the silk produced from "Bombyx selene" and other wild varieties. The true silk is lustrous and of the same color along the entire length when viewed in polarized light if single fibers *only* are observed. The raw silk may be either silvery white or yellow. The yellow is due to sericin which is a glue covering the fiber. The silkworm spins two threads which are jointed together by this sericin. The photomicrograph shows where the two threads have become separated due to the removal of some of the glue. The average diameter is about .018 m.m. A boiling solution containing 1% of neutral olive oil soap removes almost completely this sericin. Traces of it can be found, however, clinging to the fibers even after the silk has been boiled off. The weight of the silk is reduced about 25 per cent by this process.

Richardson gives the following analysis for mulberry silk:

Water	12.50%
Fats	.14%
Resins	.56%
Sericin	22.58%
Fibroin	63.10%
Mineral water	1.12%

The composition of fibroin is approximately as follows:

Carbon	48.53%
Hydrogen	6.43%
Nitrogen	18.33%
Oxygen	26.67%

Richardson suggested that the formula for fibroin might be

$$x \begin{matrix} NH-CO \\ CO-NH \end{matrix} x \qquad \text{(x is a hydrocarbon residue)}$$

Richardson's analysis gives sericin the following composition:

Carbon	48.80%
Hydrogen	6.23%
Oxygen	25.97%
Nitrogen	19.00%

It is possible to convert fibroin to sericin by the action of strong HCl, water and oxygen being absorbed.

$$\underset{\text{Fibroin}}{C_{15}H_{23}N_5O_6} + H_2O + O \longrightarrow \underset{\text{Sericin (Mulder)}}{C_{16}H_{25}N_5O_8}$$

Weighting in Silks.—Silk has a great affinity for a number of salts. They are readily absorbed and greatly increase the weight. Since raw silk is very expensive this property has been greatly abused by people who sell to the trade. Weighting may reach as high as three or four hundred per cent, especially in black silks. This decreases the tensile strength. It has been shown by Strehlenert that black silk weighted 140% has only one-sixth of the tensile

strength of raw silk. Tin phosphate and often tin silicate is used for the weighting of white and colored silks. The deterioration of the weighted silks can be lessened by the addition of glycerine or tannin, and the evil effect of the sunlight may be lessened by the addition of stannous chloride. Solutions of sodium chloride will destroy silk in twelve months if the solution is as much as .5 per cent. Stronger solutions destroy it more readily.

The weighting for the silk is either volatile or is of inorganic origin. Various solvents such as ether will remove oils and fatty acids. Tannin and glue are removed with a 2 per cent soda solution at 40°C. Sugar, dextrine and glycerol are removed by cold water. Prussian blue is decomposed with the 2 per cent soda solution. This is then acidified with HCl and ferric chloride is added. The Prussian blue will be again precipitated.

Aluminum, tin, iron, silica, and phosphoric acid may be found in the ash. The silica can be removed by mixing with the ash a fluoride and concentrated sulphuric acid. The volatile silicon fluoride can be caught in a drop of water on a slide inverted over the dish. If the drop should contain some sodium compound, crystals of sodium silicofluoride would be formed.

The remainder of the ash should be treated with hot concentrated HCl, and then diluted. H_2S will precipitate the tin as stannic sulphide, or rubidium chloride will precipitate characteristic crystals of rubidium chlorstannate. At the same time large crystals of the rubidium alum may crystallize out due to the presence of aluminum and the sulphate radical. The presence of the phosphate radical can be determined by the addition of ammonium molybdate and nitric acid. Warming helps this reaction.

Wild Silks.—Tussah is a name given to a large number of wild silks. The most important are the following:

Tussah. Obtained from Antherea mylitta in India. It is brown.

Yamamai. Obtained from Antherea yamamai in Japan. It is greenish.

Silk with Sericin
Medium wool with serrations
Tussah Silk
Beard Hair of Goat

Fig. 37.

Fagara. Obtained from Atticus Atlas in China.
Eria. Obtained in India from Atticus ricini (white).
Muga. Obtained from Antherea assama in Japan.
False Tussah. Obtained from Antherea pernyi in northern China. It is a dark brown.

Detection.—Tussah silks may be distinguished chemically by means of their insolubility in an alkaline solution of copper hydroxide. Filsinger found that true silks are readily soluble in this reagent.

Cold hydrochloric acid (Sp. gr. 1.16) dissolves mulberry silk very rapidly. Tussah silk dissolves only partly after 48 hours.

The coloring of the wild silk varies from a yellow to a dark brown and is distributed throughout the fiber. The coloring matter of cultivated silks is removed with the gum. It is not only necessary to boil off the Tussah fibers but also bleach with peroxide. Under the microscope the cross-section appears wedge-shaped. In the longitudinal directions striations run obliquely across the broad surface. The diameter is about .05 mm. This is somewhat greater than in cultivated silks and makes the fiber stronger.

Laboratory Exercises for Groups I and II

1. Examine under medium and high power specimens of raw and degummed silk. (See page 204.)
2. Examine specimens of wild silks, noting particularly the color. (See page 204.)
3. Examine various samples of wool and determine by means of the calibrated micrometer eyepiece whether the sample is fine, medium or coarse. (Measure the diameter and count the serrations.) (See page 204.)
4. If possible secure samples of wool from various parts of a sheep and compare the diameters and serrations.
5. Make the Lieberman and Molisch tests on animal fibers.

6. Test hair or wool for the presence of sulphur as described in the text.
7. Examine pieces of woolen cloth for shoddy.

Group III

Vegetable Fibers

(*Ligneous* and *Non-Ligneous*)

Ligneous.—The ligneous fibers may be identified by any one of the standard tests for lignin. Some of the most useful are given below.

1. Maule's Test. Sections are soaked for about five minutes in a one per cent solution of potassium permanganate, and after washing in water, are soaked for two or three minutes in dilute hydrochloric acid, and finally in ammonia. All lignified parts turn red.

2. Herzog's Quantitative Method. The material is very finely ground or divided. The weight of the sample taken should be from .2 to .3 grams. It should be placed in a flask on a glycerine bath and 10 c.c. of hydriodic acid (sp. gr. 1.70) added. A current of CO_2 must be used. When a substance containing the methoxyl group is heated with hydriodic acid methyl iodide is formed. The vapors are passed through a three-bulb condenser, the first bulb being empty to condense the steam, the second containing water to absorb the hydriodic acid, and the third containing red phosphorus to retain the iodine liberated by the decomposition of the hydriodic acid. The vapors of methyl iodide containing carbon dioxide are passed into a solution containing a mixture of 5 c.c. of a 40% solution of silver nitrate with 50 c.c. of 95% alcohol. The methyl iodide is precipitated as silver iodide and is weighed in the usual manner. One hundred parts of silver iodide are equivalent to 6.4 parts of methyl. The methyl value in the following table is based on that for pure lignin being taken as 52.9%. The values are taken from Matthews.[1]

[1]Textile Fibers—Matthews.

	H_2O.	Methyl value on fiber dried 100° C.	% Lignin.
Manila hemp	6.81	15.92	30.11
Jute	8.06	21.20	40.26
Coir	7.36	22.00	41.59
Vegetable silk	6.88	8.18	15.46
Aloe	7.90	9.11	17.32
Ramie	7.84	.77	1.46
Linen (Russian)	8.40	4.81	.92

3. Land uses a counter stain method for the identification of lignin. Sections from fresh material are fixed in 95% alcohol. Sections from preserved material are rinsed in alcohol or water before staining. The following summarizes the procedure:

1. Safranin, 2—24 hours.
2. 50% alcohol until differentiated.
3. Dehydrate in 95 and 100% alcohol.
4. Light green in clove oil, 3 to 30 minutes.
5. Xylol. Two or three c.c. of absolute alcohol may be added to each 100 c.c. of xylol, if the free light green shows a tendency to precipitate.
6. Mount in balsam.

Light Green Stain

Light green	1 gram
Clove oil	75 c.c.
Absolute alcohol	25 c.c.

Safranin Stain

Safranin	1 gram
95% alcohol	50 c.c.
Water	50 c.c.

Herzberg's stain will color ligneous fibers a yellow and cellulose violet to blue. (See page 224.)

Hoehnel's reagent[1] will stain ligneous fibers yellow and cellulose brown if only solution 1 is used. If solution 2 is

[1]See page 223.

applied after solution 1 is used lignin remains yellow but the cellulose becomes blue or violet.

Bast Fibers.—In making a microscopic examination of the fibers of this group, a study of the cross-section is very important. There often is a greater difference apparent in the shape and arrangement of the cells in the cross-section than in the longitudinal direction.

Bast fibers show joints or dislocations along the cell walls resembling the joints on corn or sorghum cane. They are made more prominent by treating the fibers with chlor-iodide of zinc.

A comparison of the tensile strength of some of the commercial fibers shows the importance of the bast group.

		Approximate tensile strength in kilograms per sq. mm.
Bast fibers	Hemp	78
	Jute	49
Raw silk		40
Linen		36
Cotton		34.27

Bast fibers have been classified[1] according to the size of the cell wall and inner canal.

1. The central canal takes up about four-fifths of the diameter of the fiber: Ramie and China grass (Blue with iodine and H_2SO_4).
2. The canal is two-thirds of the diameter of the fiber: Pineapple fiber, hemp, Pita and sunn hemp.
3. The canal is mostly less than one-half the diameter of the fiber: Jute, Ambari hemp, Yucca, New Zealand hemp, Manila hemp.
4. The canal is often reduced to a mere line. Linen gives only a slight test for lignin. (Blue with iodine and H_2SO_4).

All of the plant fibers show double refraction. Cotton,

[1] Matthews—Textile Fibers.

for instance, shows a gray to yellow, while the bast cells of flax and hemp show bright colors.

Jute.—Of the ligneous fibers jute and hemp are the most important, and they can be distinguished not only by means of their appearance under the microscope but also by chemical means. Jute gives a more intense color reaction with phloroglucinol and hydrochloric acid, and has stronger affinity for basic dyestuffs. Jute also has a more silky lustre.

Jute fibers are not as strong as some of the other bast fibers and they lack durability. Bleaching does not make the fibers a permanent white, consequently a yellowish color develops with age. The walls of the cells have varying thickness which also tends to weaken the fiber. The lumen seems to occupy about a third of the diameter, is often irregular, but very clearly defined. The ends of the fibers gradually taper to a point.

Hemp.—This is a bast fiber from Cannabis sativa. It is a native of Asia although a large amount is grown now in America. The world's annual production of hemp may reach 700,000,000 pounds. The hemp fiber is prepared like flax and jute, namely, rippling, retting, breaking and heckling. It is used as a substitute for linen except in the most expensive linens. Hemp may be distinguished from flax by examination of the ends of the fibers. Hemp fibers may have forked ends. Flax never does. Both have the joint-like structure so characteristic of bast fibers. The lumen is broad but becomes very narrow toward the end of the fiber. The fiber is uneven in diameter and has attached to it occasionally parenchymous tissue. In this will be found crystals of calcium oxalate. Flax does not have these crystals. Many fibers have "burette-like" ends.

Manila hemp is obtained from one of the plantings of the Philippine Islands. It is obtained from the leaf stalks by slicing them longitudinally and scraping them until the fibers are exposed. The fiber is strong, light, and easy to handle. These qualities make it important for cordage and coarse weaving. The lumen is very distinct and is very

large. The ash of manila is a dark gray. Sisal gives a white ash.

Pita hemp is made from the leaf of the aloe or century plant. The botanical name is *Agave americana*. It is very hardy and grows well even in the desert places in Mexico and South America. The leaves are large, being from eight to ten feet long and about a foot wide. Since there are about 35 of these leaves on a plant and often as many as 5000 plants per acre the yield of fiber is quite high on the basis of an acre even though a leaf yields only about 8% of the fiber. The fiber makes a very strong rope, stronger even than jute or sunn hemp. There are many varieties of hemps. Dodge lists thirty-three.

Coir is made from the shell of the cocoanut. This shell is fibrous. The green fruit is soaked for several months in water and torn apart into fibers about 8–10 inches long. It is made up into mats. The color is brown. Small silicified stigmata can be found occasionally on the fiber bundles. On ignition they are left as round silicions skeletons (Matthews). Coir has been used for caulking vessels as it rots with difficulty.

There are a large number of fibers used for textile and paper manufacture which cannot be described in a book of this nature. For a more complete description the student is referred to one of the more complete books on this particular subject.[1]

Group IV

(Vegetable fibers not responding to lignin reaction.)

Cotton (*Gossypium*).—When examined under the microscope cotton appears as a long ribbon-like band twisted around the axis several times. The inner canal (lumen) may contain air. The fibers polarize, giving gray and yellow colors. The following are the varieties of cotton showing certain physical properties as given by Dannerth.

[1]Matthews—Textile Fibers.

	Diam. in mm.	Length.	Rel. breaking strength.
Egyptian (makko)	.017	4	7.5
Peruvian	.021	3	5
Indian	.025	2.8	10
Sea Island	.009	4	8
Chinese	.025	2	
Brazilian	.018	3.5	
Upland	.019	2.5	

Of these varieties the Sea Island is the most valued variety. The Chinese, Peruvian and Brazilian are harsh but relatively strong.

Cotton will give the characteristic reactions for cellulose. Unfortunately both linen and ramie, being almost pure cellulose will also give the same color reactions as cotton. Ramie however does not have the twists in the fiber as does cotton, and linen has lines occasionally crossing the fiber which resemble the joints on a cane or bamboo stalk. Good grade of cotton should be well "twisted."

Chemical Reactions of Cellulose

Cellulose dipped in strong sulphuric acid and then thoroughly washed and dried is converted into *amyloid,* a substance that is much stronger than the original cellulose and is waterproof. This will give a blue color with iodine solution.

Dilute hydrochloric acid will weaken cotton and strong hydrochloric will destroy it.

Nitric acid (specific gravity 1.4) will increase the tensile strength 78 per cent and cause a contraction of 24 per cent. If the cotton before treating is bleached, it is exposed fifteen minutes to the acid and then washed and dried.

Nitric acid of specific gravity 1.5 will convert the cellulose into oxalic acid. A more dilute acid will convert the cellulose into oxycellulose which will react with basic dyestuffs such as methylene blue.

Cellulose treated with a mixture of nitric and sulphuric acids will be converted into collodion.

Hydrofluoric acid will convert the three members of this group into a tough, transparent and waterproof substance.

Cellulose dipped into molten organic acids such as tartaric acid will cause a rupture of the cell walls due to the crystallization of the acid, and the fiber will be very brittle.

Thymol mixed with sulphuric acid will give a violet coloration to a fiber of cellulose.

If cellulose is boiled with dilute sulphuric acid and the entire amount finally distilled over into a solution of aniline and hydrochloric acid, an intense red color will be noticed due to the presence of furfurol.

Schweitzer's solution, an ammoniacal solution of copper oxide, will dissolve cellulose.

LINEN.—Under the microscope linen shows nodes and often joint-like lines running almost straight across the fiber. Bleached linen has a silky luster. The lumen is small. Swellings are numerous.

Linen can also be distinguished from cotton by means of Frankenheim's test. If the fibers are dried and then immersed in olive oil, linen fibers will become transparent after being pressed between blotting paper. Cotton will remain opaque. Star-shaped crystals of calcium oxalate are nearly always absent from flax. They are usually found in hemp and can be used to distinguish these two fibers from each other.

LABORATORY EXERCISES FOR VEGETABLE FIBERS

1. Examine samples of raw cotton from various sources. Record the degree of natural twist, the diameter and length. Poor twist probably indicates that it was picked too green.
2. Examine samples of Sea Island cotton and compare with upland cotton.
3. Secure samples of linen. Examine the fibers for swellings and joints.
4. Note the behavior of cotton, linen, hemp, jute and ramie between crossed nicols with and without the selenite plate.

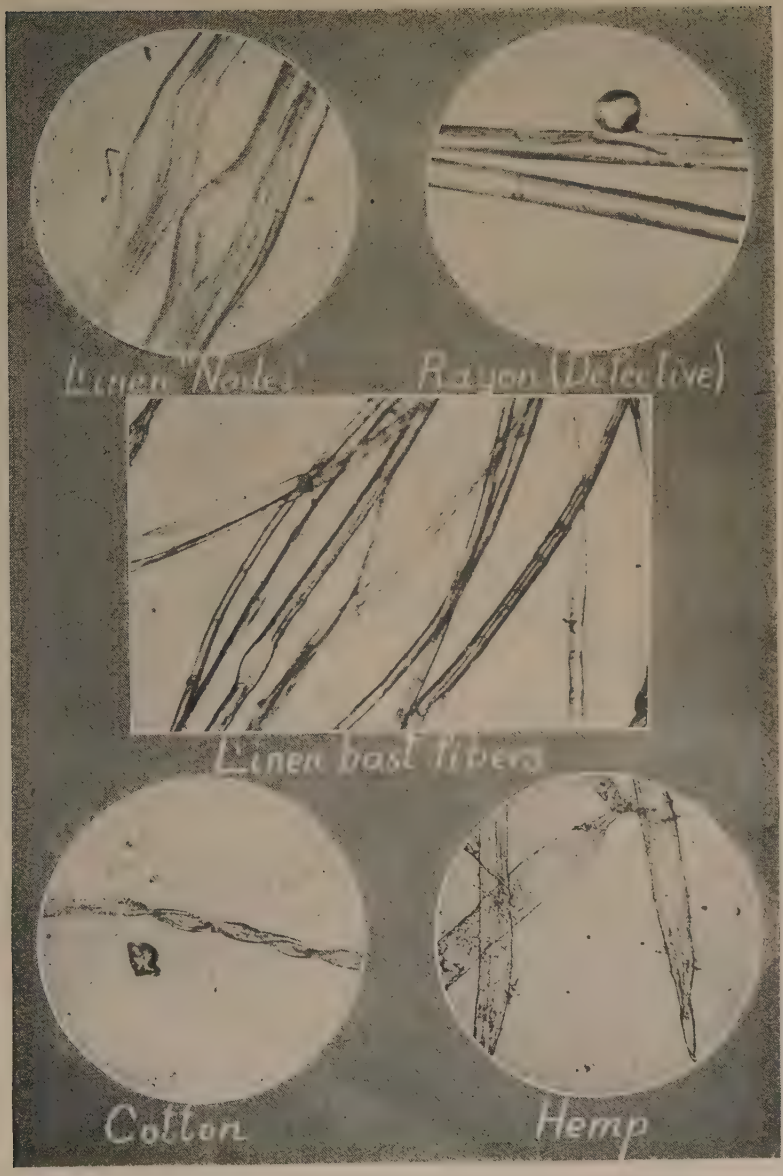

Fig. 38.

5. Examine cotton, ramie, jute, hemp and linen, measuring the size of the central canal, length and diameter of fiber. Make cross sections also.
6. Make stain tests on vegetable fibers for cellulose and lignin.

Group V

Artificial Silks (Rayons)

Rayons or artificial silks naturally fall into groups depending upon the process of manufacture.

1. Collodion Silks.—Chardonnet, Lehner's, Duvivier's. This variety will show deep striations and will give bright colors when examined between crossed nicols.

If treated with strong sulphuric acid to which has been added a fragment of diphenylamine the fibers will become a deep blue.

If brucine hydrochloride is used the fibers will become a bright red.

Collodion silk differs from viscose silk and copper silks in its ability to take up basic dyes without aid of mordants.

2. Cuprammonium Silks.—Pauly, Linkmeuer's, Thiele. Striations are faint. Diameter less than collodion silks. Polarizes well.

3. Viscose Silk.—This has deep striations, has about the same average diameter of collodion silks and does not give color tests with sulphuric acid and diphenylamine. Polarizes well.

4. Acetate Silk.—Striations are of medium depth. It gives very faint polarization colors, and in this way can be distinguished from the other varieties.

Mitchell & Prideaux give the following figures for ash content:

Collodion	2.23%
Viscose	.28%
Cuprammonium	.18%

Fig. 39.

SCHWALBE'S TESTS.—Chardonnet's silk will reduce Fehling's solution, the liquid becoming green. With Pauly and Viscose silks the solution remains blue.

If Pauly and Viscose silks are treated with a solution consisting of 20 g. zinc chloride, 2 g. potassium iodide, .1 g. iodine and 15 c.c. water, the viscose will retain a blue green color on washing, but the Pauly silk will quickly fade.

LABORATORY EXERCISES

1. Examine samples of viscose, collodion, acetate and cuprammonium silks with polarized light and selenite plate.
2. Observe also the striations, the tendency to swell in water, and the action of H_2SO_4 and diphenylamine on collodion silks.
3. Examine cross sections of each variety of artificial silk.

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CHAPTER VII

Pulp Woods and Papers

Pulp Woods.—For the convenience of the analyst trees may be grouped into two divisions.

1. Coniferous—spruce, pine, hemlock, larch, etc.

2. Nonconiferous—poplar, sycamore, aspen, cottonwood, etc.

The coniferous are called soft woods and the latter hard

Fig. 41. Western Hemlock (Radial).

woods, although in some cases a soft wood may be harder than a so-called hard wood. The coniferous tree is evergreen, bears cones and has needle-like leaves. The nonconiferous has broad leaves such as found on the maple or sycamore. The two groups are also decidedly different in their cellular structure. This difference makes it possible for the industrial analyst to determine the source of raw material which went into the manufacture of a given paper or some other commercial product.

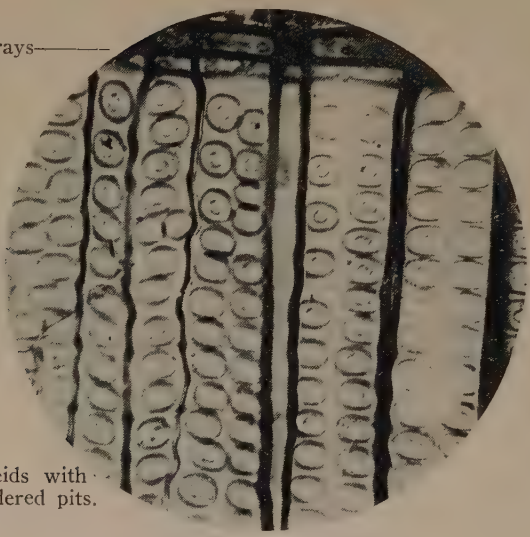

Fig. 40. TAMARACK (RADIAL).

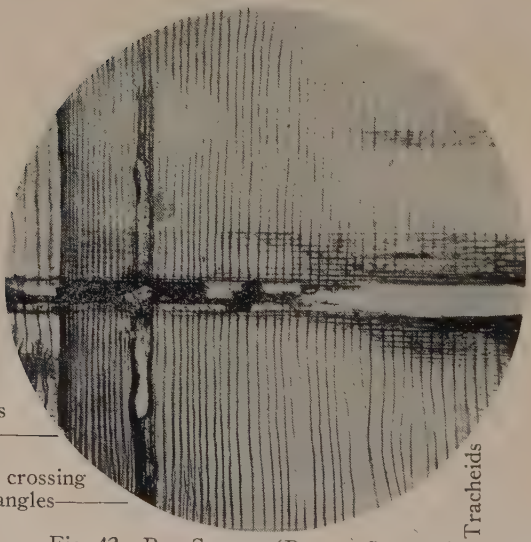

Fig. 42. RED SPRUCE (RADIAL SECTION).

Prepared sections can be purchased from any biological supply house for a nominal price, or can be prepared in the laboratory if time permits. Thin sections of twigs selected for study are made with a microtone. These are stained with saffranin or some other suitable stain and mounted on a glass slide in the usual way. If the section is cut at right angles to the length it is called a cross section, cut parallel to the radius a radial section and tangent to a radius a tangential section. The radial section offers most advantages.

Coniferous Woods.—These may be divided into two groups:

1. Conifers with resin passages—pine, spruce, tamarack, larch, and Douglass Fir.

2. Conifers without resin passages—hemlock, cypress, redwood, cedar, yew, fir.

In the photomicrograph of the radial section of red spruce two resin canals can be seen crossing each other at right angles. One of these canals is running parallel to the tracheids and the other parallel to the medullary rays. Resin cells are indicated by tiny dots in the canal. As the growing season gradually grew to a close the tracheids became leaner and a sharp line marks the place where growth ceased at the end of the growing season and started the following spring with well developed tracheids. This combination of spring and summer wood composes the annular rings of a tree. By these its age can be calculated and the climatic conditions at a definite period estimated.

Tracheids are undeveloped ducts in coniferous trees. They have tapering ends and usually show at least one row of bordered pits. They convey mineral solutions upward through the stem of the plant. Coniferous pulps can always be detected by the presence of tracheids.

Medullary rays are parenchyma cells extending radially from the cortex to the pith or from a part of the xylem to a part of the phloem. In the radial section they can be seen crossing the tracheids at right angles. They distribute

Fig. 43.
Radial section of Sycamore showing union of two tracheae.

Fig. 44.
Radial section of Black Cottonwood showing arrangement of tracheae.
(*Courtesy of Forest Service*)

radially foods brought up from the roots by the tracheids and also the elaborated sap formed in the leaves. They are a storehouse for starch, resins, alkaloids, etc.

Coniferous pulp consists mainly of tracheids and medullary rays.

Nonconiferous Woods.—The nonconiferous pulps can be distinguished by the presence of tracheae. These are arranged one above the other from the root ends on up to the leaf tips forming a continuous tube for water movements from root to leaf. Thin parts of the walls are for the passage of food materials in solution. The tracheae may be spiral, annulo-spiral, recticulate, pitted, bordered pored, or scalariform (ladder-like). Examples of these are shown in the photomicrographs of the poplar, curcubita, and sycamore. A chain of tracheae is shown in the photomicrograph of straw pulp. (See page 226.)

Paper Pulps.—No attempt can be made here to describe manufacturing processes in detail. In a qualitative way paper pulps may be classified into

1. Soda—(Nonconiferous, also spruce and hemlock).
2. Mechanical—(Coniferous, fibers torn and lacerated).
3. Sulphate—(Coniferous).
4. Sulphite—(Coniferous).
5. Miscellaneous—(Rags, rye straw, esparto, etc.).

The soda pulps are usually from poplar or some member of the poplar group. The fibers are pointed and the tracheae are characteristic. Mechanical pulp may be from spruce, hemlock or some other coniferous wood. It is badly torn, shows tracheid pits distinctly and gives a strong lignin reaction. It is difficult to distinguish between sulphite and sulphate pulps, by means of the microscope. The sulphite and sulphate fibers are not lacerated but chemical action has lessened the distinctiveness of the bordered pits. Miscellaneous materials must be identified by means of their individual characteristics. It is very essential to have present in the laboratory samples of known composition for comparison.

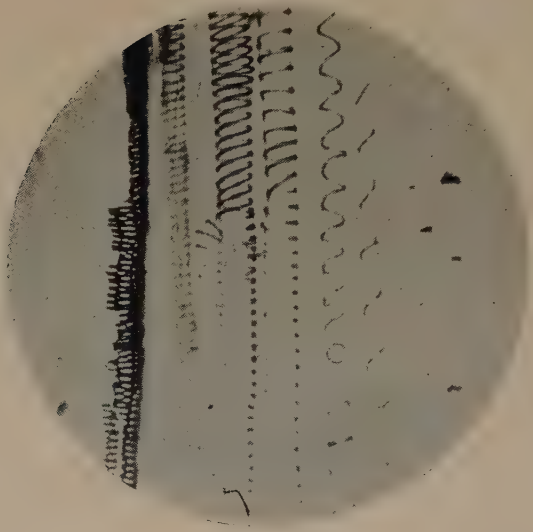

Fig. 45.
Curcubita (showing the spiral in various stages of development).

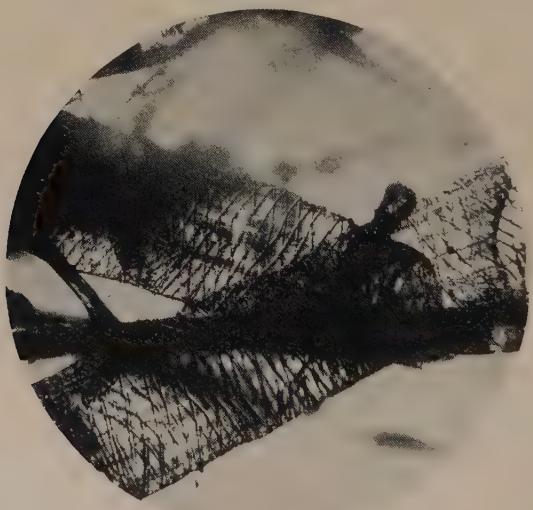

Fig. 46.
Tracheae from a sample of Poplar pulp.

Preparation of Sample.—If the sample is very small the fibers may be isolated by agitation in a small test tube with glass beads. These serve to isolate the fibers with the least injury. It is often possible to soften the paper with water in a watch glass and tease out the fibers with a sharp-pointed needle. Before any stain is added the water should be pressed from the pulp as completely as possible.

Fiber Stains.—Two of the most important reagents used for the identification of fibers are Hoehnel's reagent and Herzberg's stain. Many coal tar dyes can also be used.

Hoehnel's Reagent

Solution I. One gram of potassium iodide dissolved in 100 c.c. of water, and iodine added in excess.

Solution II. Twenty cubic centimeters of glycerol are mixed with 10 c.c. of water. Thirty c.c. of concentrated sulphuric acid are then added.

The fiber is treated with Solution I, the excess of reagent is removed with filter paper, and then Solution II is applied.

The Cornell laboratories recommend the following:

Potassium Iodide	5 grams	
Distilled water	100 c. c.	(Sol. A)
Iodine	2.85 grams	
Glycerine	5 c. c.	

Solution B. Sulphuric Acid Sp. gr. 1.45.

With Hoehnel's reagent (Solution A)

Yellow indicates mechanical wood, jute, etc. (lignin).
No Color indicates chemical wood, esparto.
Brown indicates cotton, linen, bleached hemp.

If Solution B is now applied after Solution A the following will be the color changes:

Violet—cotton, linen, bleached jute, esparto.
Blue—chemical wood, straw, esparto.
Yellow—mechanical wood, jute, manila.

If over stained the violet color may not appear. A brown coloration may be seen instead.

Herzberg's Stain (Stock Solutions)

Solution A. Dissolve zinc chloride in water until a specific gravity of 2.00 is reached.

Solution B. Water 50 c.c.; potassium iodide 30 gms.; add iodine until an excess remains after several days.

For use mix one cubic centimeter of Solution B with nine cubic centimeters of Solution A.

Herzberg's stain will color a fiber yellow, red or blue, and serves as a valuable means of placing the fiber in a

Fig. 47. Sulphite Pulp (Coniferous).

group depending upon the color reaction. The sample of paper is moistened with water and a few individual fibers are separated on a glass slide and dried. A small amount of this fiber is added to a drop of the solution and covered with a cover glass. When examined under the microscope a red color in the fiber would indicate linen, cotton, bleached hemp or manila.

A yellow color would indicate flax, manila, ramie, esparto mechanical wood, straw or any fiber carrying lignin.

A blue color would indicate chemical wood, bleached straw, esparto, jute.

Jenke's Stain

This reagent is made by mixing 50 c.c. of a saturated solution of magnesium chloride with 2.5 c.c. of a solution prepared by dissolving 23 grams of potassium iodide and 1.5 grams of iodine in 20 c.c. of water. With this reagent

Colorless or faintly reddish fibers indicate chemical wood.

Brown fibers indicate cotton, linen, hemp.

Blue or violet fibers indicate bleached straw.

Yellow—mechanical wood and unbleached jute.

Penetration of Woods by Chemicals

It is often necessary to protect wood material from the attack of minute organisms. This is done by subjecting the wood to chemical treatment. The penetration of the chemical will depend not only on the temperature and the pressure but also on the nature of the wood. If the wood has open tracheids the penetration is easier than when they are closed with tyloses, or when the wood is composed of tracheids closed at the ends. In the latter case the impregnating material must seep through the walls or through the bordered pits.

The medullary rays[1] and other parenchyma cells appear to affect the degree of penetration very little. The density of the wood matters little and the difference between summer and spring wood is of little importance. Cross-grained woods offer greater resistance than straight-grained and both radial and tangential directions are more difficult to penetrate than the longitudinal. The following hardwoods are arranged in the order of their increasing resistance to penetration by creosote.

Slippery elm	Hackberry	Sweet birch
Red oak	Tupelo gum	Red birch
Chestnut oak	Wild red cherry	White-heart beech
White ash	Basswood	Sycamore
Green ash	Silver maple	White oak
White elm	Yellow birch	Red gum

[1]Teesdale & MacLean, Bull. 606, U. S. Dept. Agr., 1918.

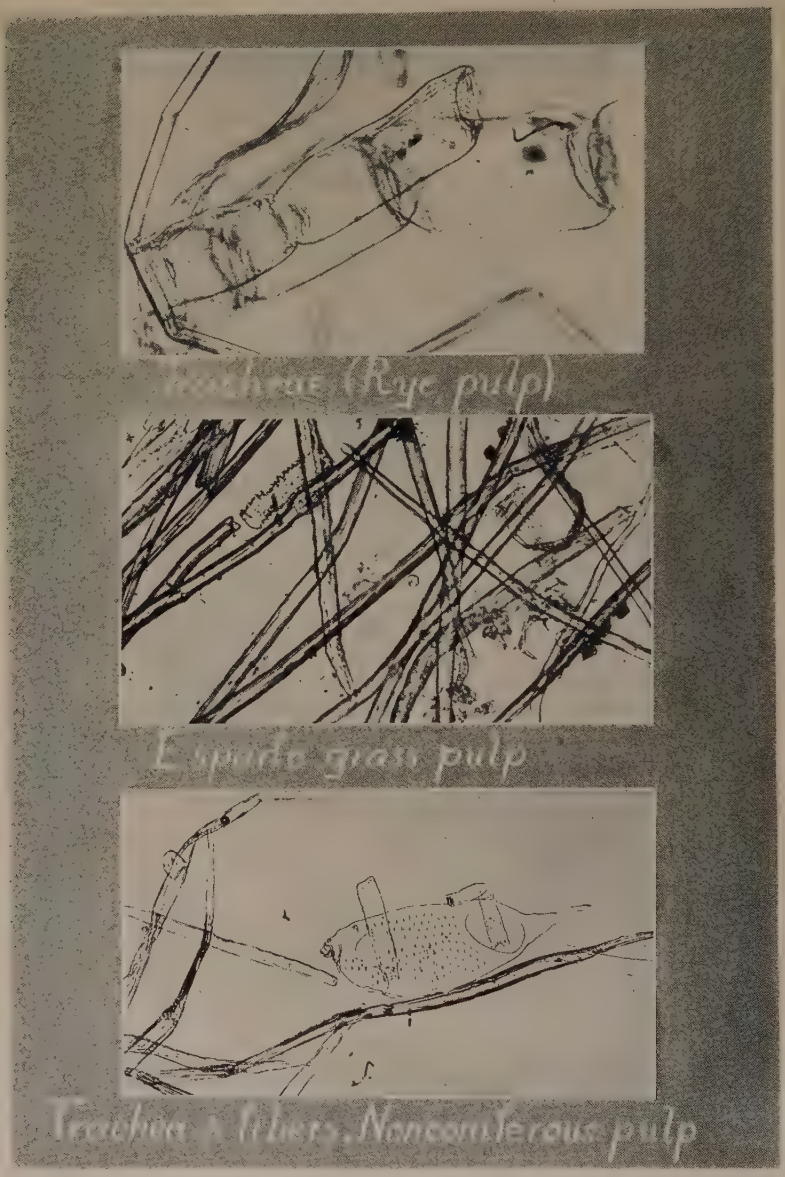
Tracheae (Rye pulp)
Esparto grass pulp
Tracheæ & fibres, Nonconiferous pulp

Fig. 48.

Laboratory Exercises for Pulps and Papers

1. Using strong illumination, examine a piece of lens paper under the microscope.
2. Moisten a piece of blotting paper, tease off a few fibers with the point of a needle. Make drawings of the fibers present.
3. Secure samples of poplar pulp and make drawings of the various fibers found.
4. Prepare pulp from newspaper and make drawings of fibers found.
5. Examine book paper for presence of starch granules.
6. Examine cigarette paper for presence of calcium carbonate. (Test the ash with a trace of dilute sulphuric acid. Slender crystalline needles are $CaSO_4.2H_2O$.)
7. If possible secure samples of the following pulps and make drawings: linen, rag, esparto, bagasse, mechanical.
8. Select some material which has not yet been commercialized for paper pulp. Prepare some pulp and report the quantity and quality of fiber found.
9. Try out the effect of stains on the various paper pulps which are available.

Bibliography

The United States Department of Agriculture, Forest Service, at Madison, Wisconsin, welcomes an opportunity to coöperate with any institution or private research. On several occasions they have loaned the writer valuable prepared slides of various wood sections, some of which were used in illustrating this book. They have prepared a list of publications on the structure and identification of wood. Some of these are free, others can be purchased at slight cost. A partial list of these is given.

Technical Notes. (Free.)

Length of Wood Fibers.
Identification of Oak Woods.
How to Distinguish Mahogany from Walnut and Red Gum.
How to Tell Birch, Beech and Maple Apart.
Identification of Pulpwoods.

MIMEOGRAPHED REPORTS. (Free.)
American Pulpwoods.
Effect of Wood Structure on Glue Penetration.
Shrinking and Swelling of Wood.
Structure of Wood.
Key for the Identification of Native Woods for Manufacture of Furniture.

BULLETINS AND CIRCULARS. (Price nominal.)
Guide-Book for the Identification of Woods Used for Ties and Timbers.
Identification of True Mahogany and So-Called Mahoganies.
Relative Resistance of Various Hardwoods to Injection with Creosote.
Ground Wood Pulp.
Grinding Spruce for Mechanical Pulp.
The Timber Pines of Southern United States, with a Discussion of the Structure of Their Wood.

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The Penetration of the Mycelium of Certain Molds Growing on Aspen, Oak, and Sitka Spruce Wood, and Some Microchemical Means for Determining It. (Eloise Gerry, American Lumberman, Jan. 7, 1922.)
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Microscopic Structure of Woods in Relation to Properties and Uses. (Eloise Gerry, Proceedings of Society of American Foresters, 8, page 159, July, 1913.)

CHAPTER VIII

Identification of Common Starches

A number of the reserve starches of plants are of commercial importance. Chemical tests are of little value in determining whether one starch has been substituted for another. Fortunately for the microscopist the starches of commerce are so unlike in size, shape and natural markings that no great skill is required to distinguish them.

Starch grains are built up in layers of soluble carbohydrates, and contain "lamellae" (rings). Aniline dyes show that these are separated by some colloidal substance like mucilage. The grains may be simple, compound or small "filler grains," lying in spaces between the larger. The point of origin of the starch grain is called the "hilum," and appears usually as a dot or cleft.

When examining starches their shape and size in microns should be noted, and their behavior under polarized light observed. The polarization cross is often characteristic, and some starches give a beautiful play of colors with the selenite plate. When stained with dilute iodine solution some starches may become indigo, others blue, purple or red. The shape and position of the hilum is important and the nature of the lamellae, whether distinct, concentric or eccentric, should not be overlooked.

For the convenience of the analyst the commercial starches may be divided into the following groups:

1. Circular starches—wheat, rye, barley, tapioca.
2. Oval starches—potato, sago, arrowroot.
3. Polygonal starches—corn, buckwheat, oat, rice.
4. Elliptical starches—legumes.

Wheat Starch.—A number of small "filler" grains are usually found. The larger circular grains are 30–45 mic-

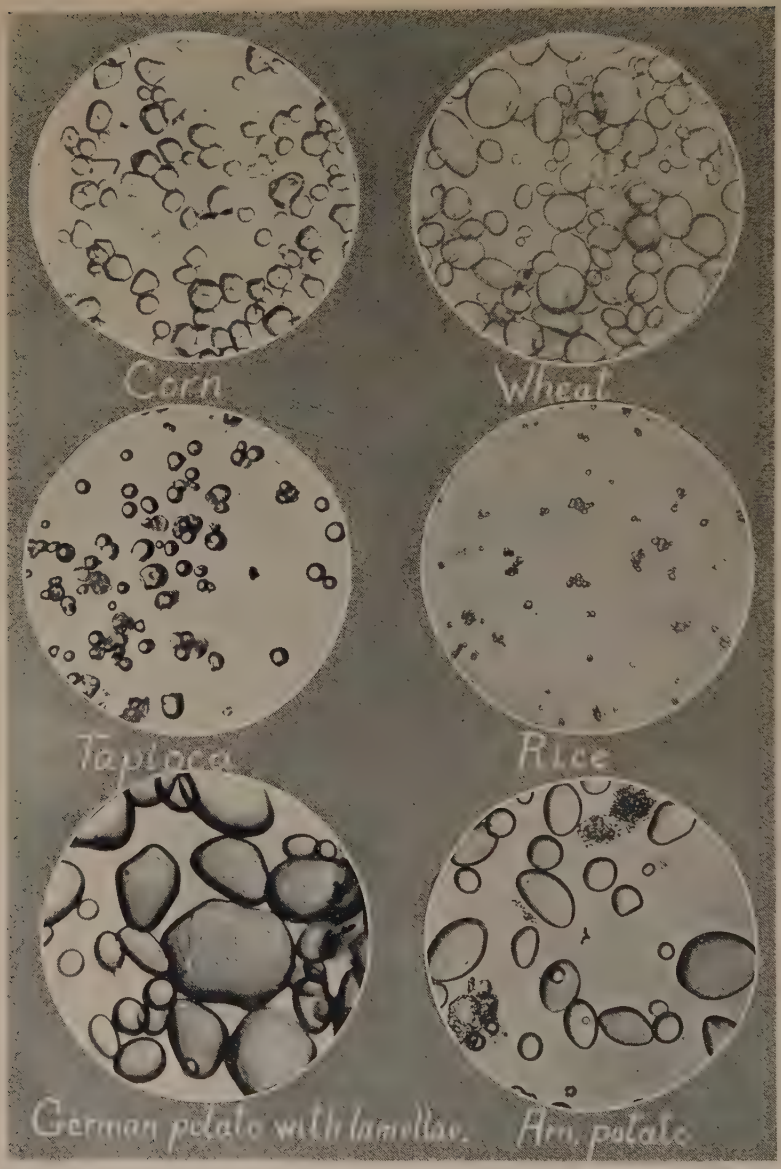
Corn
Wheat
Tapioca
Rice
German potato with lamellae.
Am. potato

Fig. 49.

rons in diameter. The hilum is an indistinct central dot. The lamellae are circular but not distinct, and polarization is feeble, giving only a faint cross, and no colors with the selenite. It is a simple starch.

Barley.—This starch is smaller than the wheat but gives a good polarization cross. The hilum may be either centric or a cleft, the lamellae usually indistinct and concentric.

Rye.—Many grains are larger than those of wheat and show a hilum with a central cleft. Some do not. The polarization cross is distinct and the lamellae concentric.

Tapioca.—Many grains are truncated and appear round if lying on their flat surface. They have a diameter of about 18 microns and a hilum consisting of a central dot.

Group II

Oval Starches

Potato.—The potato is the most common of the oval starches. Occasionally spheroidal grains can be found and two- to three-compound grains. The smallest are about 5 microns and the largest 120. The hilum, located at the smaller end of the grain, is circular and distinct, the lamellae both concentric and eccentric. The polarization cross is very distinct and the selenite plate gives bright colors.

Arrowroot.—This starch is about half as large as the potato and is simple. The hilum is near the center or towards the broad end of the grain. It may have a circular or a transverse cleft. The lamellae are indistinct but the polarization cross is clear and the selenite plate gives good colors.

Sago.—Many grains appear with cut off ends, and are irregular in shape. They may be either simple or compound. The hilum is a dot or cleft usually at the broad end. The lamellae are both eccentric and concentric and the polarization cross good. (See page 234.)

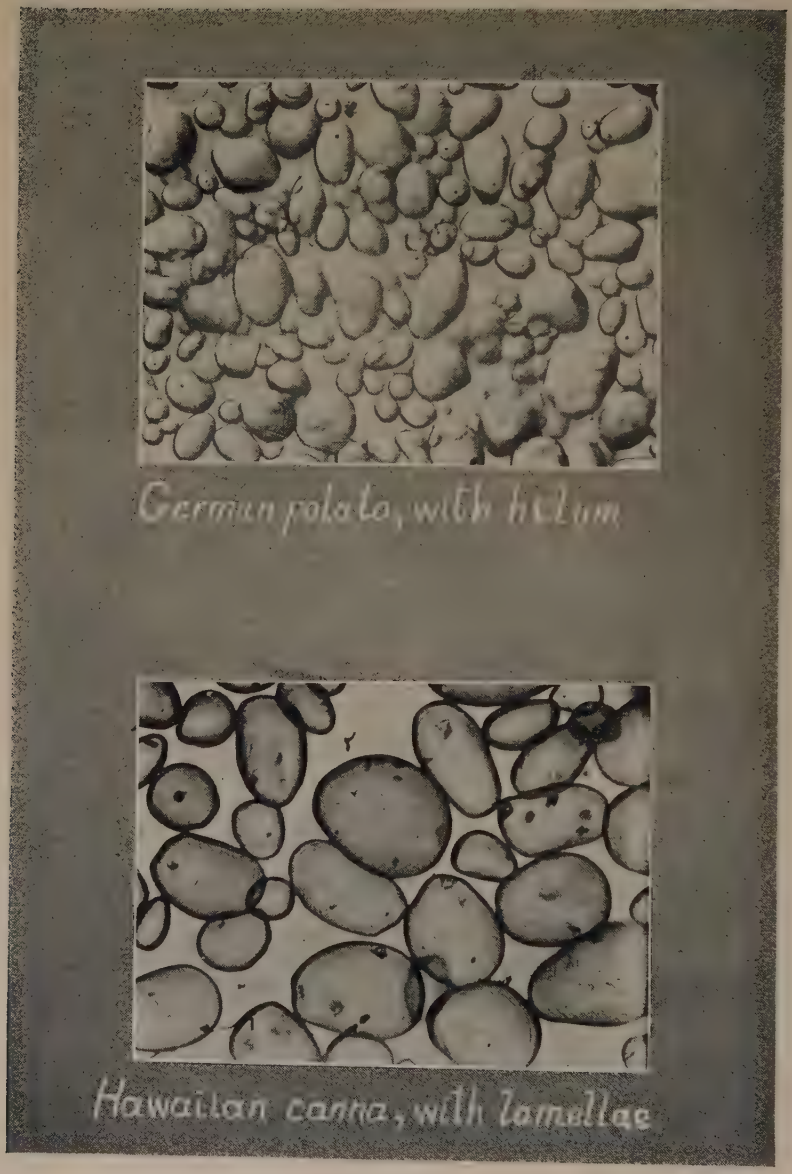

Fig. 50.

CANNA.—This is largest of the common starches, being broad and flat. The hilum is near the narrow end, the lamellae both concentric and eccentric is quite distinct when stained with weak iodine solution. It polarizes well and gives bright colors with the selenite.

GROUP III

POLYGONAL STARCHES

CORN.—Many of these grains are about 20 microns in diameter. It is simple, with faint lamellae and a hilum that is sometimes circular, sometimes cleft. It gives a good polarization cross but weak colors with the selenite.

RICE.—This is the smallest of the commercial starches, being seldom over 10 microns in diameter. The grains are usually simple but compound grains are not uncommon. Both hilum and lamellae are indistinct. The selenite produces no color play but the polarization cross is clear.

BUCKWHEAT.—The buckwheat has both simple and compound grains and is about one-half the size of corn starch. It has a central hilum, indistinct lamellae and gives a good polarization cross.

OAT.—This is smaller than the buckwheat, forms similar mass groups and has occasionally long grains.

GROUP IV

ELLIPTICAL STARCHES

BEAN.—The average length is about 40 microns. The hilum is a "clefted" elongation. The lamellae may be either distinct or indistinct. It gives polarization crosses.

PEA.—This is similar to the bean but has a less clefted hilum and more distinct lamellae.

CANNA.—This has been discussed under oval starches.

APPROXIMATE QUANTITATIVE ANALYSIS.—In the event an approximate quantitative determination of starches is

Fig. 51.

desired standard samples containing known per cents of the adulterant are made up. At least three such standards should be prepared and they should contain 2, 4 and 7% of the adulterant respectively. Each standard should be thoroughly mixed and a definite volume[1] transferred to a slide and the number of objectionable starches counted. A curve can be made by plotting the foreign particles against the known percentages. When this is done a sample of the starch under investigation is subjected to a similar examination. The average number of foreign particles occurring is noted and reference to the curve previously made gives the approximate percentage of adulteration.

Laboratory Exercises for Starches

1. Examine a small amount of fresh pulp from an irish potato. Note the location of the hilum and lamellae.
2. Prepare a *very dilute* aqueous solution of iodine. Cover a few starch granules with a drop of this solution and note the gradual darkening as the granules become blue.
3. Cover a few granules of starch with a drop of potassium bromide solution. Add to this a small drop of potassium permanganate and a trace of dilute sulphuric acid. The free bromine turns the starch a bright yellow.
4. Prepare and examine the following starches: Corn, tapioca, sweet potato, arrowroot, wheat, rice, canna.
5. Note the effect of boiling starch granules, also the changes taking place when the starch is converted into sugar by dilute acid.
6. Identify any mixture of common starches.

[1]Dr. H. S. Booth of Western Reserve University suggests the use of a brass rod with a tiny spherical depression .5 mm. deep. The rod is one inch long and 1.5 mm. thick. The depression in the end is packed with the sample which is then transferred to the object glass and carefully removed. This gives approximately the same volume each time.

CHAPTER IX

Micrometry

Calibration.—Special eyepieces, called "micrometer eyepieces," are used in microscopes for the measurement of minute substances, such as tiny beads, thickness of paint films, etc. Small disks can be purchased which carry a scale either linear or in squares. After removing the top of the eyepiece the disk is placed within. This is much less expensive than a complete micrometer eyepiece, but not so convenient.

The divisions on the scale must be calibrated against a standard stage micrometer, or something that answers such a purpose. This is a glass slide upon which has been ruled a scale with divisions .1 mm. or .01 mm. apart. This is placed upon the stage and the microscope carefully focussed. The value of the divisions in the eyepiece is determined by comparing its divisions with those on the accurately ruled stage micrometer. The value must be determined for each objective that is to be used, and the length of the drawtube should also be recorded. Although two objectives may appear to have the same magnification and may be so designated there are usually slight differences in their manufacture. This difference must be guarded against by determining the value of the divisions on the micrometer eyepiece by means of the stage micrometer for each individual objective, ocular and microscope.

Camera Lucida.—It is very convenient to use the camera lucida and sketch the object to be measured. When this has been done very carefully the preparation is removed and the stage micrometer is substituted in its place. The scale is projected on the drawing and the graduations traced. By comparing the size of the image with the graduations the length, breadth and area of the object can be found. For the detailed description of this instrument the student is referred to the catalogues of any standard optical company.

Sizing of Material.— In many branches of industry the size of the particles in the raw material or manufactured article is of paramount importance. For the examination of such materials a micrometer eyepiece ruled in squares is employed. The dimensions of these squares must be known. The material to be examined is suspended in some easily volatile liquid. A small amount of the suspension is placed on a glass slide and the liquid allowed to evaporate. This leaves the solid matter fairly evenly distributed over the surface of the glass. The preparation is examined with the calibrated micrometer eyepiece in place and the number of particles that appear to be larger than the specifications will permit are counted.

Fig. 52. Powdered Coal (showing some particles incompletely ground).

If the lens system of the microscope is such that there is little or no spherical aberration, the preparation can be thrown upon a screen by bending the microscope at right angles and using a good illumination. This greatly increases the size of the particles which in some cases can be measured with a rule.

A convenient attachment for projection work is now available from several optical companies. A small adjustable

mirror can be attached to the top of the microscope at an angle of 45° and the image projected upon a screen. When this is used it is not necessary to use a horizontal microscope. If the stage micrometer is first projected upon the screen and the squares traced permanently, the projected image of the particles under investigation can be thrown in turn upon this and measured quite accurately and with little trouble. Mr. Work of the Department of Chemical Engineering at Columbia University has found this particularly useful.

Weighing.—The micrometer eyepiece, after being calibrated, can be used in the determination of the approximate weight of many substances when the specific gravity is known, and the shape of the object under examination is such that the average length, breadth and thickness can be measured. A good experiment is with a tiny metallic bead, too small to be weighed on the balance. The bead is mounted in Canada balsam on a glass slide and covered with a thin cover glass. The average of several diameters of the bead is taken with the calibrated micrometer eyepiece and the volume calculated from the formula for spherical volume. The product of the volume and the specific gravity of the substance is the approximate weight.

$$\text{Wt.} = \text{d} \times \text{Vol. of sphere} = \frac{4}{3}\ \pi\ \text{R}^3 \times \frac{\text{d}}{1}.$$

Determination of Thickness.—This is often required in the examination of painted surfaces. The question of whether or not the contractor actually put on the agreed amount of paint per hundred square feet of surface can be very quickly determined if a small sample of the painted object is available. A cross-section of the object is placed under the microscope and the thickness of the paint film is measured in several places. The average of these several readings is taken as the thickness of the coating. Counting 231 cubic inches to the gallon it is then easy to calculate how many gallons were used per thousand square feet. The

uniformity of thickness in the coating is also important and is observed at the same time.

Analysis of Ores.—The following method is widely applicable to mixtures in general. Dr. Schneiderhöhn of Germany has used an approximate quantitative method of ore analysis with success. One of the mixtures consisted of quartz, galena and chalcocite. The ore was crushed and ground so that it would pass through a hundred mesh but catch on a hundred and twenty mesh screen. This gave the particles a uniformity of size. The sample was well mixed and then a small amount spread out on a glass slide. A counting cell assisted in the counting. The number of quartz, galena, and chalcocite particles appearing was noted and the average of about twenty fields taken. If x, y and z represent the average number of quartz, galena and chalcocite particles respectively, and d, d′ and d″ their respective densities, the percentage of each present is found from the following formulae:

$$SiO_2 \quad \text{Quartz} = \frac{dx}{dx + d'y + d''z} \times 100$$

$$PbS \quad \text{Galena} = \frac{d'y}{dx + d'y + d''z} \times 100$$

$$Cu_2S \quad \text{Chalcocite} = \frac{d''z}{dx + d'y + d''z} \times 100$$

When the percentage of galena, quartz and chalcocite is known the percentage of lead and copper can be easily figured. It is interesting to know that in test cases the method checked with the actual analysis very closely and the time consumed was only a few hours, while the older method required several days.

Laboratory Exercises

1. Place upon the stage a micrometer ruled in squares and by means of the camera lucida make a drawing of this "checker board." Grind up some hematite or other min-

eral and sift through a fine mesh sieve. Transfer a small amount of this to a slide and spread evenly. Using the camera lucida make drawings on the "checker board" you have prepared of all particles larger than the mesh of the sieve.

2. Put a 50% mixture of crushed quartz and galena through a 100-mesh sieve. Transfer small portions to a slide and average the number of particles in twenty fields. Estimate the approximate percentage of each present.

Sp. gr. of quartz	2.65
Sp. gr. of galena	7.6

3. Using the ocular micrometer which you have calibrated against the stage micrometer calculate the weight of a silver bead. Minute beads can be made by heating silver cyanide, hydroxide or nitrate before the blowpipe on charcoal. A hand lens can be conveniently used in selecting one that is very small and round. It is mounted in Canada balsam and covered with a thin cover glass.
4. Using a sharp knife, cut out a small block from a painted lead pencil. Place this upon a slide so that an edge carrying the paint film can be examined under the microscope with the micrometer ocular in place. In this way the thickness of the paint film can be calculated.
5. If possible secure splinters from boards upon which several different colored coats of paint have been placed. Measure the thickness of each coat.
6. Secure a sample of fine mesh from a standard sieve. Using the micrometer eyepiece calculate the number of mesh per inch and the diameter of the openings.

CHAPTER X

Minerals and Rocks

MINERALS

Physical Properties.—A mineral is fairly constant in composition, and mineralogists can recognize many by inspection without using routine methods. In the accurate determination of minerals, in addition to the chemical tests described in the chapter on Qualitative Analysis, the analyst makes use of such physical properties as hardness, luster, tenacity, specific gravity, fusibility, cleavage and streak color.

If the mineral is opaque and sufficiently intact the crystal system can often be determined by inspection. If crushed fragments are sufficiently transparent, the refractive index, birefringence and extinction angles are also measured. If possible interference figures are obtained and the positive and negative character of the mineral determined.

Hardness.—A series of ten minerals known as Mohs' hardness scale is used as a standard for comparison. The following are the minerals arranged in order of their increasing hardness:

1. Talc	6. Orthoclase
2. Selenite	7. Quartz
3. Calcite	8. Topaz
4. Fluorite	9. Corundum
5. Apatite	10. Diamond

If the specimen cannot be scratched with the finger nail it has a hardness of 2 or above. If it cannot be scratched with a knife its hardness is at least five, and to determine it accurately a sharp edge or point on the specimen is drawn across one or more of the standard minerals until one is found which it can just scratch. For instance, if it will

not scratch orthoclase but *will* scratch apatite its hardness lies between 5 and 6.

If sufficient pressure is exerted in making the scratch a mark due to the powder of the crushed specimen will be made on the standard. This can be easily rubbed off and should not be mistaken for a real scratch.

Color.—Only freshly broken minerals should be examined for color as many, particularly those of metallic luster become tarnished upon exposure. The streak color is determined by drawing the mineral across a piece of white unglazed porcelain called a *streak plate*. The color of the mark will be the color of the powdered mineral. The color of some minerals may vary due to whatever colored impurity may be present.

Luster.—Luster may be metallic, sub-metallic or non-metallic. If the streak is black the luster is *metallic*, such as that of silver, and the finely divided powder opaque. If the thin edges of fragments transmit a small amount of light the luster is called *sub-metallic* as in limonite. If it readily transmits light it is considered *non-metallic* and will give a colorless streak or one very light in color. Non-metallic minerals may show a silky, vitreous, resinous, greasy, pearly, or an adamantine luster such as the diamond.

Cohesion.—The molecular forces holding the crystal together are weaker in some directions than others. It will therefore break more easily along these planes of least resistance, giving smooth surfaces parallel to some possible crystal face. This is known as *cleavage*, and is considered perfect if it will act as a mirror when held close to the eye. Often cracks reveal the cleavage directions. A sharp knife blade placed upon the crystal in the direction of supposed cleavage and given a quick tap with the hammer will split the mineral along those planes of least resistance.

When cleavage is very poor and the crystal breaks in many directions at the same time as in glass, the *fracture*

is said to be *conchoidal.* If irregular surfaces are produced it is called *hackly* or *uneven,* and if it breaks in long needles it is considered *splintery.*

Cleavage may be cubic, as in galena; octahedral, as in fluorite; dodecahedral, as in sphalerite; rhombohedral, as in calcite. In the hexagonal and tetragonal systems it is considered basal when perpendicular and prismatic when parallel to the prismatic faces. It is pinacoidal when parallel to the pinacoids of biaxial crystals.

Fusibility.—This is determined by comparing the ease with which a mineral fragment about 1.5 mm. in diameter will fuse compared to the fusibility of minerals in such a series as that of the Brush-Penfield modification of Von Kobell's scale which is given below.

1. Stibnite—Large fragments fuse easily even in the luminous flame.
2. Chalcopyrite—Fragments of standard size fuse slowly in the luminous flame.
3. Almandine Garnet—Fuses readily to a globule before the blowpipe.
4. Actinolite — Edges of small fragments are readily rounded before the blowpipe.
5. Orthoclase—Edges of fragments are rounded with difficulty before the blowpipe.
6. Bronzite—Only the finest and thinnest edges can be rounded.

To determine the fusibility the fragment having a diameter about 1.5 mm. is held by means of the forceps so that the thinnest edges will be exposed to the luminous and later to the hottest point of the blowpipe flame. The beginner must first practice upon the fragments of standards in order to form a basis for comparison.

Other Heat Effects.—When intensely hot some minerals such as zircon or thorium oxide will emit a bright glow; others, such as fluorite when heated gently become

luminous. This property of *phosphorescence* is also exhibited by some minerals when exposed to sunlight and in some instances rubbed. When exposed to an electric discharge some minerals will phosphoresce and others when subjected to temperature changes may themselves become electric, being positively charged at one end and negatively at the other. This property is known as *pyroelectricity* and may be detected by means of a cat's hair. By rubbing the hair between the fingers it becomes positively charged. If it is then placed near the crystal which has been heated to about 100°C it will be drawn to the negative pole.

Specific Gravity.—The ratio of the weight of a substance to that of the same volume of water is known as specific gravity. A solid immersed in a liquid in which it is insoluble is buoyed up by the weight of an equal volume of water displaced. To determine the specific gravity of irregular solids the substance is weighed first in air and then in water, its loss in weight being carefully noted. If WA is the weight in air and Ww its weight in water the specific gravity can be calculated from the formula

$$\text{Sp. gr.} = \frac{\text{WA}}{\text{WA} - \text{Ww}}$$

If the substance is soluble in water some other liquid of known density must be substituted as the immersion liquid and the results calculated on a water basis.

If the specimen is of a porous nature, accurate measurements cannot be obtained. Minerals containing considerable impurities show variable results depending upon the nature of the foreign substances present. If accuracy is desired only pure specimens should be used.

Powders.—Very small fragments or powders may first be weighed in air, (M) then transferred to a pycnometer which has been previously weighed full of water. (W) After the powdered mineral is inserted the water is brought

up to its previous level and the new weight noted. (w) The specific gravity is then calculated from the formula

$$\text{Sp. gr.} = \frac{M}{M + W - w}$$

Smeeth[1] melted a small amount of vaseline in a watch glass and after it cooled determined the weight in water. (w′) He then poured off the water and removed traces of moisture with filter paper. The vaseline was again heated up and the weighed sample of mineral powder (w) mixed in. The weight of the mixture in water (w″) was determined as before and the specific gravity calculated from the equation

$$\text{Sp. gr.} = \frac{w}{w - (w'' - w')}$$

Use of Heavy Liquids.—If the specific gravity is not too high small mineral fragments can be floated on some heavy liquid. By adding carefully another liquid of low specific gravity, a mixture can finally be obtained in which the particle apparently neither sinks nor swims. The specific gravity of the solid and liquid mixture is then approximately the same and can be measured by a Westphal balance. The two liquids should be miscible in all proportions.

The following heavy liquids have been used for some time with satisfactory results. They can also be used for the mechanical separation of the various components of crushed rocks.

Thoulet Solution — (Sp. gr. 3.1). Dissolve 230 grams KI and 270 grams of HgI_2 in 80 c.c. of cold, distilled water. It is then warmed on a water bath until a tourmaline crystal floats. It can be diluted with water to a density approaching 1.0.

[1]On a Method of Determining the Specific Gravity of Substances in the Form of Powder. Proc. Roy. Dublin Soc., VI (1888-1890), 61-62.

ROHRBACH SOLUTION—(Sp. gr. 3.55). Shake together 100 parts BaI_2 and 130 parts HgI_2 and then add 20 grams of water. Place the preparation on an oil bath previously heated to about 175° and stir well until dissolved. Then pour into a porcelain dish and concentrate until a crystal of topaz (3.55 Sp. gr.) will float. *The liquid is very poisonous* and does not stand dilution very well.

BRAUNS SOLUTION — A solution of methylene iodide (CH_2I_2) was used by Brauns in 1886. At a temperature of 17°C it has a specific gravity of 3.3221. At lower temperatures it increases gradually until at 5° it becomes 3.3485. At 74°C it decreases to 3.189. It can be diluted with benzol but not with water or alcohol.

OTHER SOLUTIONS—Bromoform (Sp. gr. 2.88) has been suggested by Schroeder van der Kolk.

Acetylene tetrabromide ($CHBr_2$—Br_2HC) was used by Muthmann. (Sp. gr. 3.) It can be diluted with ether or benzol.

Thallium formiate (Saturated solution) varies in density with the temperature as follows: (Clerici.[1])

C°		C°	
10	3.14	60	4.32
20	3.40	70	4.50
30	3.64	80	4.67
40	3.87	90	4.76
50	4.11	95	Floats Ilemite

APPROXIMATE DENSITY.—The specific gravity of small fragments can also be approximately determined by comparison. A small glass tube about eighteen inches long and about six millimeters in diameter is closed at one end and filled with water or some denser liquid if necessary. A fragment of the mineral whose density is to be determined is dropped in and also one whose density is known. The

[1]Enrico Clerici: Preparazione di liquidi per la separazione dei minerali. Riend. Acad. Lincei. Roma (Ser. 5), XVI (1907), 1 Semsetre, 187-195.

open end is corked and the tube quickly inverted. The mineral that is heavier will fall quicker. Different minerals of known specific gravity can be substituted until one is found which will fall at approximately the same time as the unknown. Under these conditions the density of both should be approximately the same. The following minerals are convenient standards.

Brucite	2.39	Anglesite	6.35
Calcite	2.72	Pyromorphite	6.5-7.1
Magnesite	3.00	Zinc	7.0
Apatite	3.15	Iron	7.3-7.5
Rhodochrosite	3.5	Cinnabar	8.1
Sphalerite	4.10	Copper	8.85
Smithsonite	4.30	Bismuth	9.8
Molybdenite	4.75	Silver	10.5
Hematite	5.00	Lead	11.37
Zincite	5.5	Mercury	13.6
Cuprite	6.	Gold	19.3

BALANCES.—The common balance for the determination of specific gravity has one pan with a chain shorter than the other. Attached to the under side of this pan is a hook upon which a second pan can be attached. When weight in air is desired the sample is weighed in the upper pan with the lower one immersed in a beaker of water. When weight in water is wanted the specimen is placed in the lower pan.

Very accurate determination can be made with the *Jolly balance*. This consists of an upright post about a meter high upon the front of which is a scale in millimeters extending vertically. The top of the apparatus carries a hook upon which one end of a coil spring may be fastened. The lower end of the spring carries two balance pans, one attached to the bottom of the other. The relative weights in air and water are indicated by the lengthening of the spring when the mineral is placed in the top and later in the bottom pan, the difference in the lengthening of the spring showing the buoyant effect of the water.

Beam balances, such as Rodgers for solids and the Westphal type for liquids or solids are very satisfactory. If necessary the specimen can be weighed on an ordinary laboratory balance, and pans attached to the balance beam so that one weight can be obtained of the specimen immersed in water.

SUBLIMATES.—Sublimates of minerals deposited on charcoal by means of the blowpipe are important. The finely divided mineral is mixed with sodium carbonate and placed in a small hole made in a charcoal stick. The flame of the blowpipe is then directed upon the assay at first gently to keep from blowing the specimen away. As fusion begins to take place greater heat may be employed. The specimen will be either infusible, completely volatile, fumes may escape, a sublimate may be deposited near the assay, or a metallic bead result. The following are characteristic.

ANTIMONY—A white sublimate near the assay.

ARSENIC—A white sublimate higher up on the charcoal than antimony.

TELLURIUM—A white sublimate of TeO_2 resembling antimony oxide.

SULPHUR—Odor of SO_2. In a closed glass tube a yellow sublimate of sulphur may be obtained.

BISMUTH—An orange sublimate which may be white at some distance from the assay. The bismuth bead is brittle.

ZINC—Gives a yellow coating when hot and white when cold. The reducing flame must be used. On adding a drop of cobalt nitrate solution and again heating the preparation becomes green.

SELENIUM—This gives a reddish sublimate and a disagreeable odor.

(*Beads*)

IRON—Many iron compounds heated with charcoal in the reducing flame become magnetic.

COPPER—Roasting many copper compounds in the reducing flame with charcoal in the flux will give metallic copper.

LEAD—This gives a permanent yellow sublimate of PbO near the assay. The lead bead is easily malleable, and has a dull appearance.

SILVER—This gives a permanent bright metallic bead, harder than the lead in malleability tests.

GOLD—Easily fusible to a yellow bead.

TIN—Easily fusible to a bright bead. White coating if heated intensely.

PREPARING THIN SECTIONS.—It is sometimes very necessary to examine thin sections of a rock or mineral. Sections may be cut by means of special saws or chips may be secured and ground down by hand. Various types of cutting machines are described in equipment catalogues. Some are arranged for both grinding and sawing, being driven by either hand or electric power. Saws of thin tin disks set with diamond chips are available for about ten dollars. Some have a smooth edge and the diamond dust moistened with olive oil or petroleum is fed directly. When mechanical equipment is not available recourse must be had to hand grinding. For this smooth metal or glass plates are convenient. Plates of cast iron are recommended for rough grinding and plate glass for fine work.

At least three grades of emery or carborundum dust are needed. No. 120 carborundum for coarse grinding is followed by No. 180, and the last careful grinding done with emery FFFF. When a suitable chip is obtained a small amount of No. 120 carborundum is placed upon a smooth cast iron plate that is kept wet. The specimen is placed upon this and at first considerable pressure can be exerted by the finger tip as the chip is moved with a circular motion here and there on the grinding plate. Grinding at one spot on the plate must be avoided as an uneven surface in time would result. When a smooth surface has been developed

on the chip it should be washed well and brushed carefully to remove any of the 120 carborundum. It is then transferred to a second plate which carries the No. 180 carborundum. This is also kept wet and the grinding repeated as before and the specimen again rinsed and brushed carefully. The final finish to the surface is done with FFFF emery dust on a third plate. No scratches from the 180 carborundum should remain. After rinsing this face is mounted upon a glass slide by means of Canada balsam that has been previously warmed. After the cement has hardened the other face is ground down in a similar manner. At this time great care must be observed as the section becomes thin. If the specimen is ground too long with 180 carborundum it will be ground completely away.

Good specimens should be ground down to about .03 mm. in thickness, so thin that fine print can be read through them. By observing the interference color some idea of the thickness can be obtained, and if the microscope is equipped with a graduated fine adjustment the thickness can be measured by focussing first on the object glass and then upon the top of the specimen.

Specimens soluble in water must be ground with some liquid in which they are insoluble.

For material such as coal Harris* suggests soaking first in turpentine and then in dilute Canada balsam. Gentle heat is applied gradually hardening the balsam and then the coal ground down in the same manner as rock specimens.

Tables.—Space will not permit a description of all of the known minerals that exist, the number of which is approximately sixteen hundred. Many of these are very rare and can be found in the more complete tables in books devoted exclusively to mineralogy. Some of the most important in commercial use are carried in the tables which follow. If the beginner becomes familiar with the pro-

*C. L. Lord and W. H. Harris: Cutting Sections of Coal. Science Gossip, 1882, 136-137.

cedure in the determination of these more common minerals it is believed that he will be able to use the tables in more complete works intelligently.

Laboratory Exercises

1. Prepare the sublimates of arsenic, antimony and lead oxide.
2. Prepare lead, silver and bismuth beads from galena, argentite and bismuthinite respectively. Try their malleability.
3. Note that compounds of antimony and arsenic with sulphur may be completely volatile.
4. Be able to judge if a mineral fragment has a fusibility above or below 5.
5. Determine the hardness of ten minerals and check your findings with the values in the tables.
6. Determine the specific gravity of six minerals and check your results against the values in the tables.
7. Determine the hardness of ten minerals.
8. Examine the streaks of several minerals and learn to identify color.
9. Become familiar with luster of minerals.
10. Examine the following for cleavage:

Galena - - - - - - Cubic	Stibnite - - - Pinacoidal
Arsenopyrite - Prismatic	Argentite - - Conchoidal

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OPAQUE MINERALS WITH METALLIC OR SUB-METALLIC LUSTER

(Easily fusible)

NAME	Composition	Streak	Hardness	Sp. Gr.	Fusibility	Crystal System
Graphite	Carbon	Black	1+	2.2	.....	H
Molybdenite	MoS_2	Black	1+	4.75	.....	H?
Lead	Pb	Gray	1.5	11.37	1	I
Stibnite	Sb_2S_3	Dark	2.0	4.55	1	O
Bismuthinite	Bi_2S_3	Gray	2.0	6.5	1	O
Argentite	Ag_2S	Dark	2+	7.3	1.5	I
Tellurium	Te	Gray	2.3	6.1	1	H
Galena	PbS	Dark	2.5	7.6	2	I
Chalcocite	Cu_2S	Dark	2.5	5.7	2+	O
Silver	Ag	Shiny	2.5	10.5	2	I
Bismuth	Bi	Shiny	2.	9.8	1—	H
Pyrolusite	MnO_2	Black	2.	4.75	.....	.....
Bornite	Cu_5FeS_4	Dark	3.	5+	2.5	I
Antimony	Sb	Black	3+	6.6	1	H
Arsenic	As	Gray	3.5	5.7	1	H
Tetrahedrite	$4Cu_2S.Sb_2S_3$	Black	3.5	4.8	1.5	I
Siderite	$FeCO_3$	Light	3.5	4.4	.....	H
Cuprite	Cu_2O	Reddish	3.5	6.0	2.5	I
Manganite	$MnO(OH)$	Brown	4.0	4.3	.....	O
Stannite	$Cu_2S.FeS.SnS_2$	Black	4.0	4.4	1.5	Massive
Niccolite	NiAs	Brown	5.	7.5	2	H
Arsenopyrite	FeAsS	Black	5.5	6.0	3	O
Cobaltite	CoAsS	Black	5.5	6.0	2.5	I

OPAQUE MINERALS WITH METALLIC OR SUB-METALLIC LUSTER—CONT'D

(Fusible with difficulty)

NAME	Composition	Streak	Hardness	Sp. Gr.	Fusibility	Crystal System
Pyrolusite	MnO_2	Black	2.+	4.75	High	.....
Goethite	$FeO(OH)$	Brown	5.5	4.3	5+	O
Limonite	$2Fe_2O_3.3H_2O$	Brown	5.5	3.6	5+	.....
Wolframite	$(Fe,Mn)WO_4$	Black	5.5	7.2	3.5	M
Chromite	$FeCr_2O_4$	Brown	5.5	4.6	.....	I
Ilmenite	$FeTiO_3.Fe_2O_3$	Black	5.5	5+	High	H
Psilomelane	$MnO_2.BaO.K_2O$	Black	5.5	4.3	High	.....
Franklinite	$Fe,Zn,MnO(FeMn)_2O_3$	Black	6.0	5.15	High	I
Magnetite	Fe_3O_4	Black	6.0	5.18	5+	I
BRONZE AND YELLOW MINERALS						
Orpiment	As_2S_3	Yellow	1.5	3.48	1	M
Gold	Au	Yellow	2.5	19.3	2.5	I
Chalcopyrite	$CuFeS_2$	Dark	3.5	4.2	2	T
Bornite	Cu_5FeS_4	Dark	3.0	5.	2.5	I
Millerite	NiS	Black	3+	5.6	1.5	H
Pyrrhotite	$Fe_{11}S_{12}$	Black	4.0	4.65	2.5	H
Limonite	$2Fe_2O_3$	Brown	5.5	3.6	5.	.....
Pyrite	FeS_2	Black	6.0	5—	2.5	I
Marcasite	FeS_2	Gray	6.	5	2.5	O

OPAQUE MINERALS WITH METALLIC OR SUB-METALLIC LUSTER—CONT'D

RED AND BROWN MINERALS

NAME	Composition	Streak	Hardness	Sp. Gr.	Fusibility	Crystal System
Realgar	AsS	Reddish	1.5	3.5	1	M
Cinnabar	HgS		2+	8.1	1.5	H
Proustite	$3Ag_2S.As_2S_3$		2+	5.55	1.	H
Pyrargyrite	$3Ag_2S.Sb_2S_3$	Reddish	2.5	5.85	1.	H
Crocoite	$PbCrO_4$		2.5	6.0	1.5	M
Minium	Pb_3O_4		2.5	4.6	1.5	.....
Copper	Cu	Shiny	2.5	8.85	3.0	I
Vanadinite	$Pb_4(PbCl)(VO_4)_3$		3.0	7.0	1.5	H
Cuprite	Cu_2O	Reddish	3.5	6.0	2.5	I
Hematite	Fe_2O_3	Brown	5.5	5.2	5+	H

BLUE AND GREEN MINERALS

Malachite	$(Cu.OH)_2CO_3$	Green	3.5	4	3	M
Azurite	$(Cu.OH)_2(CuCO_3)_2$	Blue	3.5	4	3	M
Atacamite	$Cu_2Cl(OH)_3$	Green	3+	3.75	3+	O
Chalcanthite	$CuSO4.5H_2O$	Blue	2.5	2.2	3	T

Non-Opaque Isotropic Minerals Which Show No Change When Rotated Between Crossed Nicols

(Arranged in order of increasing refractive indices—Modified arrangement of Esper Larsen.)

n	*Name*	*Amorphous Crystalline*	*Hardness Sp. Gr.*	*Remarks*
1.323	Villiaumite NaF	C	H 3.5 G 2.79	Red. Sol. in H_2O. Add bismuth sulphate and a trace of nitric acid and get needles.
1.406	Opal $SiO_2.nH_2O$	Amorphous	H 6.00 G 1.9-2.3	Sol. in NaOH. Then add ammonium fluoride. Get crystals Na_2SiF_6.
1.434	Yttrocerite $(Y,Er,Ce)F_3.5CaF_2.H_2O$	C	H 4 to 5 G 3.5	Blue. Infusible. Sol. in acid.
1.434	Fluorite CaF_2	C	H 4 Sp. G. 3.18	Fusible 1.5. Soluble in acid. Add trace of H_2SO_4 and get needles $CaSO_4$.
1.456	Alum $K_2O.Al_2O_3.4SO_3.24H_2O$	C	H 2.00 G 1.76	Sol. in H_2O. Gives tpyical alum crystals; also gives six-sided plates with $Bi_2(SO_4)_3$ and needles with $CaCl_2$.
1.457	Yttrofluorite $(Ca_3Y_2)F_6$	C	H 4.5 G 3.55	Yellow. Fusible. Sol. in acid. Gives needles with sulphuric acid.
1.483	Sodalite $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$	C	H 6.00 G 2.2	Nitric acid solution gives white ppt. with silver nitrate.
1.487	Analcite $Na_2O.Al_2O_3.4SiO_2.2H_2O$		H 5.00 G 2.25	Decomposed by HCl. Add to it a crystal of RbCl and a trace of H_2SO_4 and get alum crystals.
1.490	Sylvite KCl	C	H 2.00 G 1.99	Sol. in water. Gives white ppt. with $AgNO_3$ and six-sided plates with bismuth sulphate.
1.50	Lazurite $3Na_2O.3Al_2O_36SiO_22Na_2S$		H 6.00 G 2.4	Azure blue. Boiled with HCl will give sulphide test with lead acetate paper or with sodium nitroprusside.
1.509	Leucite $K_2O.Al_2O_3.4SiO_2$	C	H 5.50 G 2.47	Hydrochloric acid soln. gives tests for aluminum with a trace of H_2SO_4 and RbCl. (Alum crystals). Reacts for K with H_2PtCl_6.

NON-OPAQUE ISOTROPIC MINERALS WHICH SHOW NO CHANGE WHEN ROTATED BETWEEN CROSSED NICOLS—CONTINUED

n	*Name*	*Amorphous Crystalline*	*Hardness Sp. Gr.*	*Remarks*
1.52	Pollucite $2Cs_2O.2Al_2O_3.9SiO_2.H_2O$	Cubes	H 6.5 G 2.90	Decomposed by HCl. This solution gives alum crystals with sulphuric acid. It also gives yellow octahedra with H_2PtCl_6.
1.535	Succinite Hydrocarbon	Amor.	G 1.07	Soft. Yellow amber. Easily fusible.
1.544	Halite NaCl	Cubes	H 2.5 G 2.17	Gives white ppt. with $AgNO_3$. Gives needles with $Bi_2(SO_4)_3$.
1.59	Garnierite $(Ni,Mg)O.SiO_2.nH_2O$		H 2.00 G 2.60	Decomposed by HCl. The solution made alkaline with ammonia gives a pink color with dimethyl glyoxime. Gives the triple nitrite reaction, for nickel.
1.642	Sal Ammoniac NH_4Cl	C	H 1.5 to 2.00 G 1.53	Will sublime. Sol. in water. Sublimate will give test for NH_4 (yellow octahedra) with H_2PtCl_6 in water soln. Test also for chlorides.
1.69	Thorite (altered) $ThO_2.SiO_2.nH_2O$	C	H 4.5 to 5 G 5.2 to 5.4	Green, orange, black. Sol. in HCl. Gives the reactions for Rare Earths described above.
1.723	Spinel $MgO.Al_2O_3$	C	H 8.00 G 3.60	Crush very fine and fuse with sodium carbonate. Treat then with HCl. Test the solution for aluminum with RbCl and H_2SO_4. Test also for Magnesium as a $MgNH_4PO_4$. Red, green, blue, etc.
1.737	Danalite $3((Fe,Zn,Mn)O.3GlO.3SiO_2$ $Fe,Zn)S$ Octahedral Color red to gray.	C	H 6.00 G 3.43	Sol. in HCl. Evap. soln. to dryness. Test part of residue with $K_2Hg(CNS)_4$ for zinc. A hanging drop of sodium nitroprusside reacts for H_2S. Lead acetate paper is blackened. The solution reacts for iron with KCNS. It reacts for glucinum as oxalate, and also manganese.
1.780	Almandite $3FeO.Al_2O_3.3SiO_2$	C	H 7.00 G 4.04	Dark red. Becomes magnetic after heating in reducing flame of blowpipe. Soluble in HCl after fusion. Gives a strong test for iron with KCNS, and for aluminum with RbCl and H_2SO_4—alum.

NON-OPAQUE ISOTROPIC MINERALS WHICH SHOW NO CHANGE WHEN ROTATED BETWEEN CROSSED NICOLS—Continued

n	*Name*	*Amorphous Crystalline*	*Hardness Sp. Gr.*	*Remarks*
1.780 1.820	Gadolinite on heating $GlO.FeO.Y_2O_3.2SiO_2$	C	H 6.5 to 7.00 G 4.0 to 4.5	Sol. in HCl. Gives oxalate test for Yttrium and glucinum. Black.
1.83	Lime CaO	C	H 3 to 4 G 3.32	Quickly soluble in acid. Gives bundles of needles with dilute sulphuric acid.
2.05±	Limonite $Fe_2O_3.nH_2O$	Amor.	H 4.00 G 3.80	Soluble in HCl. Ocher yellow to brown. Gives red color when KCNS is added to HCl solution.
2.061	Cerargyrite $AgCl$	C	H 1.00 to 1.5 G 5.55	Fusibility 1. Soluble in ammonia.
2.07	Chromite $FeO.Cr_2O_3$	C	H 5.5 G 4.5	Spinel Group. Iron black. Gives a green color to a salt of phosphorous bead. It becomes magnetic on being intensely heated with sodium carbonate on the charcoal. It must be very finely divided.
2.16	Manganosite MnO	C	H 5 to 6 G 5.18	Emerald green. Soluble in acid. Nitric acid solution will give a violet color with sodium bismuthate or lead dioxide. Oxalic acid gives manganese oxalate crystals.
2.20	Bismutite $Bi_2O_3.CO_2.nH_2O$	Amor.	H 4 to 5 G 7	Effervesces with acid. Fusibility 1.5. The solution in sulphuric acid gives characteristic crystals with sodium chloride, forming needles.
2.20	Thorianite $ThO_2.U_3O_8$, etc.	Cubes	H ..... G 9.32	Almost opaque.
2.18 red 2.39 blue	Bunsenite NiO	C	H 5.5 G 6.4	Sol. in acid. Infus. Make the triple nitrite test for the presence of nickel, which gives a rose red. Also test the solution with dimethyl glyoxime (make alkaline with NH_4OH)

NON-OPAQUE ISOTROPIC MINERALS WHICH SHOW NO CHANGE WHEN ROTATED BETWEEN CROSSED NICOLS—CONTINUED

n	*Name*	*Amorphous Crystalline*	*Hardness Sp. Gr.*	*Remarks*
2.36	Franklinite $(Zn,Fe,Mn)O.(Fe,Mn)_2O_3$	C	H G 6.00 5.00	Iron black. Sol. in hot HCl. Evaporate some of this solution to dryness. Test one part for zinc with ammonium mercuric thiocyanate. Test the other for manganese in a neutral solution with oxalic acid; and in an HNO_3 solution with sodium bismuthate it will become pink.
2.37 Li 2.34 Na	Sphalerite ZnS	C	H G 3.5 to 4 4.0	Color light yellow to dark. Dissolve in HCl. Evaporate to dryness. Add a drop of water and test for zinc with potassium mercuric thiocyanate.
2.419	Diamond C	C	H 10.00 G 3.52	Infusible. Insol.
2.849	Cuprite Cu_2O	C	H 3.50	Streak crimson, soluble in pure sulphuric acid. Evap. to dryness, and test the slightly acid solution for copper with potassium mercuric thiocyanate, yellow crystals.
> 2.72	Tetrahedrite $5Cu_2S,2ZnS.2Sb_2S_3$	C	H 3.00 G 4.6	Decomposed by nitric acid. F 1.5. This soln. evaporated to dryness will give characteristic crystals for zinc and copper with ammonium or potassium mercuric thiocyanate. It will also give a white sublimate of Sb_2O_3 when heated on the charcoal. This dissolved in acid and then the solution diluted will give a white ppt,—indicating antimony.

Non-Opaque Minerals That Give Parallel Extinction Between Crossed Nicols

ORTHORHOMBIC, HEXAGONAL and TETRAGONAL CRYSTALS

(Arranged in order of increasing refractive indices.)

Refractive Index

1.40 Chrysocolla — H 2.00
$CuO.SiO_2.nH_2O$ — Green — G 2.00

Decomposed by acids. This solution evaporated to dryness and then treated with a drop of water and potassium mercuric thiocyanate will give yellow needles. See Copper.

1.0 red Covellite — Hexagonal — indigo — H 1.5 to 2.00
1.45 Na Cu_2S — positive — blue — G 4.6
1.80 Tl — Streak—dark — F 2.5

Soluble in nitric acid, giving a blue solution. The gases coming from the reaction will turn lead acetate paper black—sulphides.

1.433 — Orthorhombic — H 2.00
1.461 Epsomite — Negative — G 1.751
1.455 $MgO.SO_3.7H_2O$ — F 1.00
$2V=52°$

This is quite soluble in water. It gives test for sulphates.
It also gives test for magnesium in an alkaline solution of ammonium hydroxide with sodium phosphate and ammonium chloride.

1.466 — Orthorhombic — H 2.7
1.494 Carnallite — Positive — G 1.6
1.475 $KCl.MgCl_2.6H_2O$ — F 1 to 1.5
$2V=70°$

Gives test for magnesium. Gives test for potassium. Sol. in H_2O.

Hexagonal Habit — H 4.5 — Color, white
1.482 Chabazite — Cubic — G 2.1 — to flesh red.
1.480 $(Ca,Na_2)O.Al_2O_3.4SiO_2$ $6H_2O$ — F 3.0

2V Small. This is one of the Zeolites. It is decomposed by HCl. Evaporate the solution to expel excess HCl. Then test for aluminum. Also test for calcium, and for sodium.

1.480 — Orthorhombic — H 5.00
1.493 Natrolite — Positive — G 2.25
1.482 $Na_2O.Al_2O_3.3SiO_2$ $2H_2O$ — $2V=63°$ — F 2.00

This is soluble in concentrated hydrochloric acid with the separation of gelatinous silica. The filtrate from this can be tested for aluminum, and for sodium. Little or no precipitate should be obtained with ammonium oxalate for calcium, nor should many needles of calcium sulphate appear when testing for aluminum as an alum.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index

1.486 Analcite — Isometric — H 5.5
1.487 $Na_2O.Al_2O_3.4SiO_2.2H_2O$ — G 2.27
F 3.5

This is decomposed by concentrated HCl. Evaporate this after filtering off this silica, and test for the presence of sodium, and for the presence of aluminum.

1.334 Niter — Orthorhombic — H 2.00
1.506 $K_2O.N_2O_5$ — Negative — G 2.10
1.505 — F 1.00
$2V=7°$

Soluble in water. This solution will give a multitude of needles of "nitron nitrate" when acidified with acetic acid and treated with a solution of "nitron." It has a salty taste.

1.54 Ozocerite — Orthorhombic ? — H 1.00
1.515 Hydrocarbon — Positive — G .9
F Easy

It burns. It is insoluble in acids.

1.518 Hatchettite — Orthorhombic — H 1.00
1.588 $C_{28}H_{78}$ — Positive — G .96
1.523 $2V=33°$ — F at 80°C

Soluble in oils. Insoluble in acids.

1.553 Quartz — Hexagonal prisms — Positive — H 7
1.544 SiO_2 — and pyramids — G 2.66
Infusible

Insoluble in acids. The pulverized material is soluble in hot caustic alkali. Test for silicon.

1.580 Brucite — Trig. — H 2.5 Colorless
1.559 $MgO.H_2O$ — Positive — G 2.4
Infusible

Soluble in acids. Gives test for magnesium.

1.564 Beryl — Hex. — H 8.00 Colorless
1.568 $3GlO.Al_2O_3.6SiO_2$ — G 2.66 Green
Infusible Blue

Fuse with sodium carbonate. Digest the assay in HCl. Test for glucinum, and for aluminum.

1.592 Alunite — Trig. — Tab. or cubic — H 4.00
1.572 $K_2O.3Al_2O_3.4SO_3.6H_2O$ — Positive — G 2.60

It decrepitates on ignition. It is then soluble in acid. Evaporate to remove the excess acid and test for potassium; for sulphates; for aluminum.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index				
1.571	Anhydrite	Orthorhombic	H 3.00	
1.614	$CaSO_4$	Positive	G 2.93	
1.576	2V=42°		F 3.00	

Soluble in HC. Evaporate to expel the excess acid and test for calcium, and for sulphates.

1.575	Beryl	Hex.		
1.581	(See n 1,568)			

1.336	Soda Niter	Trig	H 2.00	White
1.587	$Na_2O.N_2O_5$	Negative	G 2.27	
			F 1.00	

Soluble in water. Gives test for nitrates. Gives test for sodium.

.....	Biotite	Mon. Hex. plates	H 3.00	
1.600	$K_2O.4(Mg,Fe)O.2(Al,Fe)_2O_3$	Neg.	G 2.7-3.1	
	$6SiO_2.H_2O$		F Difficult	

Mica Group. Decomposed by H_2SO_4.

1.614	Calamine	Orthorhombic	H 5.00	
1.636	$2ZnO.SiO_2.H_2O$	Positive	G 3.5	
1.617			F 6.0	
	2V=46°			

Gelatinizes with HCl. Filter off the silica, expel the excess acid and test for zinc.

1.619	Topaz	Orthorhombic	H 8.00	
1.627	$2(AlF)O.SiO_2$	Positive	G 3.58	
1.620	2V=49°—66°		Infusible	

Slightly attacked by sulphuric acid. It gives a reaction for fluorine when heated in a bulb tube with sodium metaphosphate.

1.622	Celestite	Orthorhombic	H 3.5	
1.631	$SrO.SO_3$	Positive	G 3.96	
1.624	2V=51°		F 3.00	

It is insoluble in acid. After intense ignition before the blowpipe it gives an alkaline reaction with moistened tumeric paper. Some of the powdered substance fused with sodium carbonate and charcoal will give a test for sulphides with a bright silver coin, or with sodium nitroprusside. The fused mass is soluble to some extent in HCl. Expel the excess acid and test for strontium.

1.631	Apatite	Hex. Prism. Negative	H 5.00	
1.634	$9CaO.3P_2O_5.Ca(F,Cl)_2$		G 3.20	
			F 5.00	

This is soluble in acid. Expel excess acid and test for phosphates; for calcium; for chlorides.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index					
1.636	Barite	Orthorhombic	H	3.00	
1.648	$BaO.SO_3$	Positive	G	4.50	
1.637	$2V=37\frac{1}{2}°$		F	3.00	

Insoluble in acid. Fuse with sodium carbonate and charcoal, thus reducing sulphates to sulphides. Add HCl and test for sulphides with sodium nitroprusside.

1.697	Dioptase	Trig.	H	5.00	Green
1.644	$CuO.SiO_2.H_2O$	Positive	G	3.05	
				Infusible	

Gives gelatinous silica with HCl. Expel the excess acid and test for copper.

1.486	Calcite Trig.	Negative	H	3.00	
1.658	$CaO.CO_2$		G	2.715	
					White, may be colored.
				Infusible	

Effervesces in acid. Test the solution for calcium.

1.662	Boracite	Orthorhombic	H	7.00	White
1.673	$6MgO.8B_2O_3.MgCl_2$	Positive	G	2.95	
1.667			F	2.00	

Isometric above 265°C. Sol. in acid. Expel excess acid and test for manganese, and for boron.

1.520	Strontianite	Orthorhombic	H	4.00
1.667	$SrO.CO_2$	Negative	G	3.70
1.667	$2V=7°$		F	Difficult

Soluble in acids. Note effervescence. Test for strontium.

1.665	Enstatite	Orthorhombic	H	5.50
1.674	$(Mg,Fe)O.SiO_2$	Positive	G	3.20
1.669			F	6.00
	2V 80°	Insol. in HCl		

Pyroxene. Fuse with sodium carbonate. Digest in HCl, and after filtering off the silica test for iron, and for magnesium.

1.529	Witherite	Orthorhombic	H	3.00
1.677	$BaO.CO_2$	Negative	G	4.3
1.676	$2V=16°$		F	2.5

Soluble in dilute HCl. Note any effervescence. Test the solution for barium.

1.662	Olivine	Orthorhombic	H	7.00	Green
1.699	$2(Mg,Fe)O.SiO_2$	Positive	G	3.30	Brown
1.680	2V=large		F	Difficult	

It is soluble in HCl. Yields gelatinous silica. Filter off the silica, expel the excess acid and test for magnesium, and for iron.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—CONTINUED

Refractive Index				
1.500	Dolomite	Orthorhombic	H 4.00	White
1.681	$CaO.MgO.2CO_2$	Negative	G 2.87	
			Infusible	

Does not effervesce in cold dilute acid. After expelling the excess acid test for calcium, and for magnesium.

1.531	Aragonite	Orthorhombic	H 4.00	
1.686	$CaO.CO_2$	Negative	G 2.94	
1.682			Infusible	

Soluble in dilute acid. Stains when boiled with a solution of $Co(NO_3)_2$, calcite does not.

.....		Orthorhombic	H 5.5	Green
.....	Bronzite	Positive	G 3.3	
1.685	2V=90°		F 6.0	

Pyroxene. Insoluble in acid. Same as Enstatite, n, 1.669.

1.641	Tourmaline	Hexagonal	H 7.00	Black
1.637	$Na_2O,(Fe,Mg,Cr)O,Al_2O_3$		G 3.3	Pleoc.
	SiO_2,B_2O_3,H_2O		Fusible	

Insoluble in acid. Fuse with sodium carbonate, digest in acid, filter off the silica, and test for boron; for chromium, and for aluminum.

1.723	Willemite	Trig.	H 5.5	White
1.694-5	$2ZnO.SiO_2$	Positive	G 3.9	Red
			Infusible	Green
				Yellow

Dissolve in HCl. Filter off the excess silica and expel the excess acid. Test for the presence of zinc.

1.509	Magnesite	Trig.	H 3.5-4.00	
1.700	$MgO.CO_2$		G 2.96	
			Infusible	

Soluble in hot acid. Expel excess acid and test for magnesium.

1.705	Vesuvianite	Tetragonal	H 6.5	
1.708	$2(Ca,Mn,Mg,Fe,O$	Negative	G 3.4	Pleoc.
	$(Al,Fe)\ (OH?F)O.2SiO_2$		F 3.0	

It is soluble in acid after ignition. Filter off the silica, expel the excess acid and test for iron; for manganese; for aluminum; for calcium, and for fluorine.

1.702	Diaspore	Orthorhombic	H 7.00	Colorless
1.750	$Al_2O_3.H_2O$	Positive	G 3.4	Violet
1.722			Infusible	Pleoc.

Insoluble in acid.

1. Pulverize the mineral. Make it into a paste with cobalt nitrate and ignite on charcoal—blue.
2. Digest some of the pulverized mineral with KOH, test for aluminum as cesium alum.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index

1.736 Staurolite — Orthorhombic — H 7.00
1.746 $2FeO.5Al_2O_3.4SiO_2.H_2O$ — Positive — G 3.70
1.741 — Infusible
2V=88° — Pleoc.

Slowly attacked by H_2SO_4. Often twinned. Fuse the finely pulverized mineral with $KHSO_4$ and sodium carbonate. Then digest in acid and test for iron, and for aluminum.

1.747 Chrysoberyl — Orthorhombic — H 8.5
1.757 $GlO.Al_2O_3$ — Positive — G 3.6
1.748 2V=45° — Infusible

Fuse with sodium carbonate. Digest with acid, and expel the excess. Then test for glucinum (beryllium), and for aluminum.

1.760 Corundum — Trig. — H 9.00 — Red, blue, etc.
1.768 Al_2O_3 — G 4.0
Insol. in acid. — Infusible

Fuse with sodium carbonate. Dissolve in acid. Expel the excess acid and test for aluminum.

1.618 — Trig. — H 5.00
1.818 Smithsonite — Negative — G 4.40
$ZnO.CO_2$ — Infusible

Soluble in acid. Note any effervescence. Expel the excess acid and test for zinc.

1.597 Rhodochrosite — Trig. — H 4.00 — Pink
1.817± $MnO.CO_2$ — Negative — G 3.70
Infusible

Soluble in acid. Note any effervescence. Expel the excess acid and test for manganese.

1.615 Siderite — H 4.00
1.849 $FeO.CO_2$ (See n 1.30) — G 3.80

1.633 Siderite — Trig. — Negative — H 4.00 — Gray
1.875 $FeO.CO_2$ — G 3.89 — Yellow
Infus. — Brown

Soluble in acid. Test for iron.

1.877 Anglesite — Orthorhombic — H 3.00
1.894 $PbO.SO_3$ — Positive — G 6.30
1.882 2V=60°-70° — F 1.5

Slowly soluble in HNO_3. Gives test for lead; for sulphates. Fuse with sodium carbonate and charcoal. A lead globule forms.

1.934 — Tetrag. Positive — H 5.00 — White
1.918 Scheelite — G 6.12 — Yellow
$CaO.WO_3$ — F 5.00 — Brown
Gray

Digest in concentrated HCl, and filter off the WO_3 (Yellow). Digest this in sodium hydroxide, and test for tungsten.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index

1.750 α
1.92 } γ Carnotite — Orthorhombic — Negative — H Soft — G ------- — F ------- — Yellow
1.95 }
$K_2O.2UO_3.V_2O_5.8H_2O$
1.895 }
1.925 } β 2V=39°-44°

Digest the finely divided mineral with sodium hydroxide. Test for uranium; for vanadium.

1.968 Zircon — Tetrag. — H 7.5 — Yellow
1.923 $ZrO_2.SiO_2$ — G 4.5 — Brown
Infusible

Fuse with sodium carbonate, digest in acid, filter off the silica and test for zirconium; or treat the finely divided powder with HF.

2.093 Cassiterite — Tetrag. — H 6-7
1.997 SnO_2 — G 6.8-7.1
Infusible

Fuse with sodium carbonate and charcoal, and obtain a globule of tin. Test for tin.

2.029 Zincite — Hex. — Positive — H 4.00 — Deep red
2.008 ZnO — G 5.68
Infusible

Sol. in acid. Test for zinc.

1.82 Bismite — Hex. — Neg. — H Soft — White
2.01 $Bi_2O_3.3H_2O$ — G 4.36

Soluble in nitric acid. Test for bismuth.

1.950 Sulphur — Orthorhombic — H 2.00 — Yellow
2.240 S — Positive — G 2.06
2.043 2V=69° — F 1.00

Burns with a blue flame, giving off SO_2.

2.042 Pyromorphite — Hex. prismatic — H 4.00 — Resinous
2.050 $9PbO.3Pb_2O_5.PbCl_2$ — G 7.00
F 1.5 — Pleoc.

Soluble in HNO_3. Test for lead; for chlorides.

1.804 Cerrusite — Orthorhombic — H 3.00 — Colorless
2.078 $PbO.CO_2$ — Negative — G 6.5 — White
2.076 2V=8° — F 1.5

It is soluble in dilute nitric acid. Note any effervescence. Test for lead.

2.00 }
2.35 } Li. TeO_2 — Orthorhombic — Negative or Positive — H 2.00 — White — G 5.90 — Fusible
2.18 }
2V about 90°

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—Continued

Refractive Index				
2.18 2.35 2.27	Descloizite $4(Pb,Zn)O.V_2O_5.H_2O$	Orthorhombic Neg.	H 3.50 G 6.0 F 1.5	Red Brown Black

This is soluble in dilute HNO_3. Expel the excess acid, and test for zinc; for vanadium.

2.09 2.26 2.24	Tungstite $WO_3.H_2O$	Orthorhombic Negative	H 2.5 G 5.52	Yellow to Green

This is soluble in KOH. Test for tungsten.

2.17 2.31 2.29	Geothite $Fe_2O_3.H_2O$	Orthorhombic Negative	H 5.00 G 3.8 Infusible	Yellow

Sol. in HCl. Test for iron.

2.304 2.402	Wulfenite $PbO.MoO_3$	Tetrag.	H 3.00 G 6.9 F 2.0	Colorless Yellow Orange

Decomposed by HCl. Test for molybdenum; for lead.

2.529 2.506	Greenockite CdS	Hex.	H 3-3.5 G 5.00 Infusible	

Sol. in HCl. Test the escaping gas for sulphides. Test the solution for cadmium.

2.583 2.741 2.586	Brookite TiO_2 $2V=30°$	Orthorhombic Positive	H 6.00 G 3.9 Infusible	Brown Black

Insoluble. Fuse with borax and then dissolve in HCl with tin. A violet color indicates titanium.

2.535 2.665	Litharge PbO	Tetrag. Neg.	H 2.00 G 9.13 F 1.00	Reddish

Soluble in HNO_3. Test for lead.

2.903 2.616	Rutile TiO_2 (See n 2.586)	Tetragonal, Positive	H 6.00 G 4.24 Infusible Pleoc.	Yellow Red

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3.201 2.854 3.146 2.819 Li	Cinnabar HgS	Hex.	H 2.0 G 8.1	Cochineal red.

Digest in aqua regia and test for mercury.

NON-OPAQUE MINERALS THAT GIVE PARALLEL EXTINCTION BETWEEN CROSSED NICOLS—CONTINUED

Refractive Index					
2.711	Proustite	Trig.	H	2.5	Scarlet
2.979	$3Ag_2S.As_2S_3$		G	5.8	
			F	1.0	

Decomposed by HNO_3. Test the solution for silver; for arsenic.

2.94 }	Li Hematite	Trig.	H	5.00	Black
3.01 }	Fe_2O_3		G	5.20	

Sol. in acid. Test for iron.

3.194	Stibnite	Orthorhombic	H	2.00	Lead gray.
4.303	Sb_2S_3	Neg.	G	4.6	
4.046	$2V=26°$		F	1.0	

Sol. in HCl. Test for antimony.

Monoclinic and Triclinic Minerals Which Give Oblique Extinction When Examined Between Crossed Nicols

Refractive Index n						
.....	Cryolite	Positive	Mon.	H	2.5	Soluble in H_2SO_4
.....	$3NaF.AlF_3$			G	3.00	
1.364		$2V = 43°$		F	2.00	
	It gives test for sodium. It gives test for aluminum.					
1.447	Borax	Negative	Monocl.	H	2.00	
1.472	$Na_2O.2B_2O_3.10H_2O$			G	1.70	Soluble in H_2O
1.474		$2V = 39°$		F	1-1.5	
	Test for sodium; test for boron.					
1.412	Trona	Negative	Mon.	H	3.00	Soluble in H_2O
1.540	$3Na_2O.4CO_2.5H_2O$			G	2.13	White
1.492				F	1.5	
	Test for carbonates; for sodium.					
1.444	Gaylussite		Mono.	H	2-3	Soluble in acid
1.523	$Na_2O.CaO.2CO_2.5H_2O$	Negative		G	1.94	
1.516		$2V = 34°$		F	1.5	
	Test for sodium; for calcium; for carbonates.					
1.520	Gypsum	Positive	Mon.	H	1.5-2	
1.530	$CaO.SO_3.2H_2O$			G	2.32	Soluble in HCl
1.523		$2V = 58°$		F	2.5-3	
	Test for sulphates; for calcium.					
1.518	Orthoclase	Negative	Mon.	H	6.00	Insoluble in acids.
1.536	$K_2O.Al_2O_3.6SiO_2$	$2V = 0°—70°C$		G	2.56	Color varied, usu-
1.524				F	5.00	ally white.
	Fuse with sodium carbonate. Digest in acid and expel the excess. Test for potassium; for aluminum.					
1.522	Microcline	Negative	Tric.	H	6.00	Green, pink,
1.530	$K_2O.Al_2O_3.6SiO_2$	$2V = 83°$		G	2.56	white, etc.
1.526						
	Test as above for microcline.					
1.525	Albite	Positive	Tric.	H	6.00	White
1.536	$Na_2O.Al_2O_3.6SiO_2$	$2V = 74°$		G	2.605	Insoluble
1.529				F	4.00	
	Fuse with sodium carbonate. Digest in acid and expel the excess. Then test for sodium; for aluminum.					
1.516	Chalcanthite	Negative	Tric.	H	2.5	Blue
1.544	$CuO.SO_3.5H_2O$	$2V = 56°$		G	2.2	Soluble in water
1.540				F	3.0	
	Test for copper; for sulphates.					

MONOCLINIC AND TRICLINIC MINERALS WHICH GIVE OBLIQUE EXTINCTION WHEN EXAMINED BETWEEN CROSSED NICOLS—Continued

Refractive Index						
1.539	Oligoclase	Negative	Tric.	H	6.00	
1.547	?	$2V = 86°$		G	2.64	
1.543				Infusible		

Insoluble in acid. Test as for the other feldspars.

1.541	Biotite	Negative	Mon.	H	3.00	Pleoc.
1.574	$K_2O.4(Mg\ Fe)O.2(Al,Fe)_2O_3$			G	3.00	Black
1.574	$6SiO_2.H_2O$			F	Difficult	

Decomposed by sulphuric acid. Test for potassium; alumium; iron.

1.561	Kaolinite	Negative	Mon.	H	2.00	
1.567	$Al_2O_3.2SiO_2.2H_2O$	$2V = 68°$		G	2.6	
1.565				Infusible		

Insoluble in acids. Fuse with sodium carbonate. Digest in HCl, and filter. Test filtrate for aluminum.

1.575	Chrysocolla	Negative	?	H	2.00	Green
1.598	$CuO.SiO_2.nH_2O$			G	2.4	
1.597				Infusible		

Decomposed by acid. Test for copper.

1.539	Talc	Negative	Mon. ?	H	1.00	White
1.589	$3MgO.4SiO_2.H_2O$	$2V = 6\text{-}30°$	Ortho.	G	2.7	Soluble in acids
1.589				F	2.5	

Test for magnesium.

1.561	Muscovite	Negative	Mon.	H	2.00	Mica
1.594	$K_2O.3Al_2O_3.6SiO_2.2H_2O$	$2V = 40°$		G	2.9	Insoluble in acid
1.590				F	5.7	

1.586	Colemanite	Positive	Mon.	H	4.00	Soluble in hot HCl
1.614	$2CaO.3B_2O_3.5H_2O$	$2V = 56°$		G	2.42	
1.592				F	1.5	

Test solution for calcium; for boron.

1.576	Anorthite	Negative	Triclinic	H	6.00	Feldspar Group
1.588	$CaO.Al_2O_3.2SiO_2$	$2V = 77°$		G	2.7	
1.584				F	5.00	

Gelatinizes in acid. Test for calcium.

1.61	Turquoise	Positive	Tric.	H	5.00	Blue, green
1.65	$CuO.3Al_2O_3.2P_2O_5.9H_2O$	$2V = 40°$		G	2.84	Pleoc.
1.62				Infusible		

Soluble in acid after ignition. Test for copper, and for phosphates.

1.611	Actinolite	Negative	Mon.	H	6.00	Pleoc. Green.
1.636	$CaO.3(Mg,Fe)O.4SiO_2$	$2V = 78°$		G	3.15	An amphibole.
1.627				F	4.00	

Insoluble in HCl.

MONOCLINIC AND TRICLINIC MINERALS WHICH GIVE OBLIQUE EXTINCTION WHEN EXAMINED BETWEEN CROSSED NICOLS—Continued

Refractive Index					
1.610	Glauconite	Negative	Mon.	H 2.00	Pleoc.
1.628	$K_2O.Fe_2O_3.4SiO_2.nH_2O$	$2V=20°$		G 2.2-2.8	
1.628				F Easy	Digest in acid

Test for potassium; for iron.

1.629	Hornblende	Negative	Mon.	H 6.00	Green-black
1.652	Silicate of Al, Fe, Mg,	$2V=84°$		G 3.00	Pleoc.
1.642	Ca, & Na.			F 3-4	

Insoluble in acid.

1.625	Datolite	Negative	Mon.	H 5.00	Colorless
1.669	$2CaO.2SiO_2.B_2O_3.H_2O$	$2V=74°$		G 3.0	
1.653				F 2-2.5	

Gelatinizes in acid. Test for boron; for calcium.

1.660	Spodumene	Positive	Mon.	H 6.5	Pyroxene
1.676	$Li_2O.Al_2O_3.4SiO_2$	$2V=58°$		G 3.2	White, yellow,
1.666				F 3.5	green, violet.

Insoluble in acids.

1.664	Diopside	Positive	Mon.	H 5-6	Colorless
1.694	$CaO.MgO.2SiO_2$	$2V=59°$		G 3.28	
1.671				Infusible	

Insoluble in acid.

1.661	Hornblende	Negative	$2V=84°$ Mon.	H 6	Pleoc.
1.683	Silicate of Al, Fe, Mg, Ca, Na			G 3.3	Green
1.673				F 3-4	Black

Insoluble in acid.

.....	Gadolinite	Positive	Mon.	H 7.00	Black, brown.
.....	$2GlO.FeO.2Y_2O_3.2SiO_2$	$2V=85°$		G 4-4.5	
1.70				Infusible	

Gelatinizes in acid. Test for Gl.

1.712	Cyanite	Negative	Tric.	H 4-7	Pleoc.
1.728	$Al_2O_3.SiO_2$	$2V=82°$		G 3.5	Blue
1.720				Infusible	

Insoluble in acids.

1.726	Rhodonite	Positive	Tric.	H 6.00	
1.737	$MnO.SiO_2$	$2V=$large		G 3.67	Red, pink.
1.730				F 2.5	

Slightly soluble in acid. Test for Mn.

1.730	Azurite	Positive	Mon.	H 3.5-4	
1.838	$3CuO.2CO_2.H_2O$	$2V=68°$		G 3.80	Pleoc.
1.758				F 3.0	

MONOCLINIC AND TRICLINIC MINERALS WHICH GIVE OBLIQUE EXTINCTION WHEN EXAMINED BETWEEN CROSSED NICOLS—Continued

Refractive Index						
1.729	Epidote	Negative	Mon.	H	6.0	
1.768	$4CaO.3(Al,Fe)O_3.6SiO_2.H_2O$			G	3.4	Green
1.754				F	3.0	

Partly decomposed by HCl.

1.786	Monazite	Positive	Mon.	H	5.0	Pleoc.
1.837	$(Ce,La,Di)_2O_3.P_2O_5$			G	5.1	Brown
1.788				Infusible		

Digest in sulphuric acid. Test for the rare earths.

1.655	Malachite	Negative	Mon.	H	4.0	
1.909	$2CuO.CO_2.H_2O$	$2V=43°$		G	4.0	Green. Pleoc.
1.875				F	2.0	

Effervesces in HCl. Test for copper.

1.900	Titanite	Positive	Mon.	H	5.0	Pleoc.
2.034	$CaO.TiO_2.SiO_2$	$2V=27°$		G	3.5	Yellow, brown
1.907				F	3.	Colorless

Soluble in sulphuric acid. Test for titanium.

1.93	Lanarkite	Negative	Mon.	H	2-2.5	
2.02	$2PbO.SO_3$	$2V=47°$		G	6.4-6.8	White
1.99				F	2.0	

Somewhat soluble in hot dilute HCl. Test for sulphates; for lead.

2.042	Pyromorphite	Negative	Ps. Hex.	H	4.0	Pleoc.
2.050	$9PbO.3Pb_2O_5.PbCl_2$			G	6.5-7.1	White
2.050				F	1.5	Green, brown

Soluble in HNO_3. Test for chlorides; for lead.

2.26	Wolframite	Positive	Mon.	H	5-5.5	Brownish black
2.42	$(Fe,Mn)O.WO_3$			G	7.2-7.5	Pleoc.
2.32				F	3.0	

Soluble in conc. sulphuric acid. Test for tungsten; for manganese.

2.31	Crocoite	Positive	Mon.	H	2.3-3	
2.66	$PbO.CrO_3$	$2V=54°$		G	6.0	Hyacinth red
2.37				F	1.5	

Test for chromium; for lead.

2.46	Realgar	Negative	Mon.	H	1.5-2	Aurora red
2.61	AsS	$2V=40°$		G	3.56	Completely volatile
2.59				F	1.00	Pleoc.

Test for arsenic. Soluble in alkalies.

.....	Orpiment	Positive	Mon.	H	2.0	Soluble in sulphuric
.....	As_2S_3	$2E=70°$		G	3.4	acid
> 2.72				F	1.0	Yellow

Completely volatile.

Important Minerals Arranged in Order of Their Increasing Hardness

Hardness		*Sp. Gr.*
1	Talc	2.80
1	Ulexite	1.65
1	Carnallite	1.60
1–1.5	Natron	1.4–1.45
1–1.5	Graphite	2.2
1–1.5	Kermesite	4.60
1–1.5	Molybdenite	4.75
1.5–2	Realgar	3.55
1.5–2	Soda Niter	2.29
1.5–2	Sulphur	2.07
1.5–2	Sylvanite	8–8.2
1.5–2	Mirabilite	1.48
1.5–2	Erythrite	2.95
1.5–2	Vivianite	2.6–2.7
1.5–2	Orpiment	3.48
1.5–2	Tetradymite	7.6–7.3
2	Gypsum	2.32
2	Melanterite	1.9
2	Stibnite	4.55
2	Bismuthenite	6.4–6.5
2–2.5	Pyrolusite	4.75
2	Sylvite	1.9–2
2	Niter	2.1
2.5–3	Petzite	8.7–9
2.5–3	Trona	2.1
2–2.5	Epsomite	1.7–2.6?
2–2.5	Autunite	3.05–3.2
2–2.5	Borax	1.72
2–2.5	Kaolinite	1.75
2–2.5	Stephenite	6.2–6.3
2–2.5	Bismuth	9.8
2–2.5	Torbernite	3.4–6
2–2.5	Cinnabar	8.10
2–2.5	Argentite	7.3
2–2.5	Muscovite	2.86
2–2.5	Tellurium	6.1–6.3
2.5	Galena	7.6
2.5	Copper	8.85
2.5	Halite	2.13
2.5	Silver	10.5
2.5	Calaverite	9.35
2.5	Krennerite	8.35
2.5	Electrum	13–16
2.5	Chalcanthite	2.2
2.5–5	Serpentine	2.5–2.6
2.5	Cryolite	2.97
2.5	Brucite	2.39
2.5	Copiapite	2.1
2.5	Stromeyerite	6.2–6.3
2.5	Gold	19.3
2.5–3	Glauberite	2.75
2.5–3	Jarosite	3.2
2.5–3	Hessite	8.3–8.8
2.5–3	Biotite	2.8–3.1
2–3	Thenardite	2.69
2.5–3	Polyhalite	2.77
2.4–4	Chrysocolla	2.0
2.5–4	Lepidolite	2.8–2.9
3	Calcite	2.72
3	Vanadinite	6.9–7.1
3	Pearceite	6.15
3	Anglesite	6.35
3	Lepidomelane	3–3.2
3	Astrophyllite	3.3–3.4
3	Olivenite	4.4
3	Bornite	4.9–5.4
3–3.5	Antimony	6.6–6.7
3–3.5	Celestite	3.97
3–3.5	Cerussite	6.55
3–3.5	Barite	4.5
3.5	Pentlandite	4.95–5
3.5	Sphalerite	4.05
3–4	Tennantite	4.6
3–3.5	Anhydrite	2.95
3–4	Wavellite	2.33
3–4	Deweylite	2.4
3–4	Freibergite	4.7–4.9
3–4	Tetrahedrite	4.7–5
3.5	Chalcopyrite	4.2–4.3
3.5	Descloizite	6–6.10
3.5	Adamite	4.35
3.5	Witherite	4.3
3.5–4	Malachite	3.9–4
3.5–4	Strontianite	3.5–4
3.5–4	Siderite	3.85
3.5–4	Cuprite	6.00
3.5–4.5	Rhodochrosite	3.5
3.5	Azurite	3.77
3.5	Alabandite	3.95
3.5–4	Brochantite	3.9
3.5–4	Dolomite	2.85
3.5–4	Magnesite	3.0
3.5–4	Pyromorphite	6.5–7.1
2.5–4	Scorodite	3.2
3.5–4	Aragonite	2.95
3.5–4	Stilbite	2.1
4	Fluorite	3.18
4	Liberthenite	3.6–3.8
4	Stannite	4.4
4	Pyrrhotite	4.65
4–4.5	Platinum	14–19

IMPORTANT MINERALS ARRANGED IN ORDER OF THEIR INCREASING HARDINESS— CONTINUED

Hardness		*Sp. Gr.*
4–4.5	Zincite	4–4.5
4–4.5	Colemanite	2.42
4–4.5	Heulandite	2.15
4–5	Chabazite	2.05
4–5.5	Triplite	3.6–3.8?
4.5–5	Childrenite	3.20
4.5–5	Scheelite	6.05?
4.5–5	Calamine	3.45
4.5–5	Wulfenite	6.05
4.5–5	Apophyllite	2.3–2.4
5	Melilite	2.9–3.1
5	Herdenite	3.00
5	Uraninite	9–9.7
5	Apatite	3.15
5	Smithsonite	4.30
5	Pectolite	2.7–8
5–5.5	Analcite	2.27
5–5.5	Natrolite	2.25
5–5.5	Titanite	3.4–3.5
5–5.5	Wolframite	7.2–7.5
5–5.5	Niccolite	7.5
5–5.5	Datolite	2.9–3
5.5	Cerite	4.85
5.5	Troostite	4.18
5.5	Chromite	4.6
5.5	Willemite	4.00
5.5	Linnaeite	4.90
5.5	Ilvaite	4.05
5.5	Arsenopyrite	6–6.2
5.5	Limonite	3.6–4
5.5	Turgite	4.14
5.5	Cobaltite	6–6.2
5.5	Smaltite	6.3–6.5
5.5	Allanite	3.5–4.2
5–5.5	Goethite	4.35
5–5.5	Lazurite	2.4
5–5.5	Wollastonite	2.8
5–6	Hypersthene	3.4–5
5–6	Chloanthite	6.4–6.8
5.5–6.5	Opal	2.1
5–6	Augite	3.35
5–7	Cyanite	3.56
5–6	Octohedrite	3.85
5–6	Bronzite	3.2
5.5–6	Pyroxene	3.1
5–6	Diopside	3.29
5–6	Actinolite	3.00
5–6	Hornblende	3.2
5–6	Tremolite	3.00
5–6	Psilomelane	4.3
5.5–6	Tephroite	4–4.1
5.5–6	Sodalite	2.1–2.3
5.5–6	Leucite	2.45
5–6	Wernerite	2.68
5.5–6	Nephelite	2.5–2.6
5–6	Laboradorite	2.73
6	Orthoclase	2.57
6	Albite	2.62
6	Microcline	2.57
6	Oligoclase	2.66
6	Columbite	5.3–6.5
6	Arfvedsonite	3.45
6	Andesite	2.69
6	Anorthite	2.75
6	Ambligonite	3.08
6–6.5	Acmite	3.5
6–6.5	Fowlerite	3.67
6–6.5	Rhodonite	3.63
6–6.5	Zoisite	3.25
6–6.5	Rutile	4.18
6–6.5	Braunite	4.8
6–6.5	Anorthite	2.75
6–6.5	Pyrite	5.00
6–6.5	Prehnite	2.90
6–6.5	Marcasite	4.8–4.9
6.5	Vesuvianite	3.35
6.5	Fayalite	4.32
6.5	Pollucite	2.98
6.7	Epidote	3.37
6.5–7	Chrysolite	3.27
6.5–7	Spodumene	3.18
6.5–7.5	Grossularite	3.5–6
6–7	Cassiterite	6.8–7
6.5–7	Gadolinite	4.2
7	Quartz	2.65
7	Jadeite	3.33
7	Andradite	3.75–3.8
7	Boracite	2.9–3
7–7.5	Tourmaline	3.15
7–7.5	Staurolite	3.75
7–7.5	Spessartite	4.2
7–7.5	Iolite	2.60
7–7.5	Almandite	4–4.15
7.5	Zircon	4.68
7.5–8	Beryl	2.75–8
7.5–8	Chromite	7.5–8
8	Topaz	3.52
8	Spinel	3.5–3.8
9	Corundum	3.95
10	Diamond	3.52

ROCKS

These are not constant in composition, being made up of two or more minerals in varying proportions. The individual components can be observed if the specimen is examined under a low power of the microscope. Thin sections can be prepared and the various minerals detected by means of polarized light, refractive index, etc. In some instances it is possible to separate the minerals from crushed rocks by means of a magnet or by suspension in a liquid medium whose density lies between the heavier and lighter constituents. Optical and chemical tests can then be applied. Rocks are classified by Tarr as (1) Massive, (2) Banded, (3) Soft, (4) Medium Hardness, (5) Conglomerate.

Massive Rocks

(Hard Rocks, which cannot readily be scratched with a knife)

1. *Minerals That Can Be Recognized*

GRANITES—White or pink feldspar, quartz and colored minerals.

GABBRO—Pyroxene, feldspar, olivene, mica.

SYENITES—Feldspar with little quartz.

DIORITES—Hornblende or feldspar with mica.

DOLERITES—Less than 50% feldspar with some iron and magnesium.

PERIDOTITES—Pyroxene, olivene, hornblende.

EPIDOTE—Greenstone, garnet.

QUARTZITE—Fine grains, rounded and cemented together. It breaks across the grains and not around as in sandstone.

2. *Dense Rocks, With Very Fine Grains*

(Which are difficult to recognize)

FELSITES—Light colored, breaks in splinters.

BASALTS—Dark rocks, often porous, slaggy in appearance.

3. *Glassy Rocks*

OBSIDIAN PITCHSTONE PUMICE

Banded Rocks

The composition of the banded rocks is usually:

MICA—Varied in color; a mixture with other minerals is called mica-schist.

HORNBLENDE—Dark, green to black, with long crystals of hornblende.

GNEISS—Varied in color—and composition.

Soft Rocks

(Can usually be scratched with the finger nail)

CLAY—This has a greasy feel when rubbed between the fingers. It may be of several colors. It does not effervesce in acids.

MARL—This may carry a great deal of partially decomposed shell and will effervesce with acid. Sometimes green particles of glauconite can be observed.

DIATOMACEOUS EARTH—This effervesces with acid. It has a gritty feeling. The microscope may show siliceous formations of great delicacy. Some samples may contain many thousands of minute particles in a cubic inch of material.

GYPSUM—It is more compact than the clays. It is slightly soluble in hot water, giving typical crystals of calcium sulphate when observed by the microscope. It does not effervesce in acid.

TALC—This has a soft, smooth, greasy feeling. It does not effervesce in acids. It will leave a mark on cloth.

Rocks of Medium Hardness

(Hardness between a finger nail and a knife)

LIMESTONE (*Marble*)—This may be of many colors. It will effervesce rapidly in cold hydrochloric acid. Not soluble in water. The acid solution will give crystals of calcium sulphate on evaporation with a trace of dilute sulphuric acid.

DOLOMITE—This will effervesce in acid if strongly heated.

It will give a test for calcium (see page 131), and for magnesium (see page 163).

SERPENTINE—This is a waxy and greasy looking rock. It may be red, green or black. It does not effervesce. It contains much water.

Conglomerates

(This group consists of rocks made up of different components whose size is appreciable)

1. CONGLOMERATE—This is composed of *rounded* rocks from the size of a buckshot on up to particles larger than an egg. The fragments are usually bound together with a carbonate or some siliceous material. The rounded rocks are mostly quartz.
2. SANDSTONE—This is composed of either rounded or angular quartz grains ranging in size from a buck shot on down to a pin head or smaller. The cementing material is usually limestone, which may cause an effervescence with an acid.
3. AKROSE—If the very small grains are composed of feldspar instead of quartz the rock is called AKROSE.
4. BRECCIA—The pebbles composing this rock may be as large as in the conglomerate, but instead of being rounded they are *angular*.
5. VOLCANIC TUFF—This is composed of broken volcanic rocks imbedded in volcanic ash. A solid round specimen of volcanic rock is called a VOLCANIC BOMB.
6. OÖLITE—This effervesces strongly in acid. It is composed of very small grains.
7. COQUINA—This is composed of many very small shells cemented together.

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